

# Inelastic Collision and Three-body Recombination

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# Inelastic Collision and Three-body Recombination

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*To my wife,*

*Yilian Zhang,*

*for her endless support.*

*Life has given me the chance, ice cold, like the flash of the blade.*

*—myself*

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## SUMMARY

The three body inelastic recombination coefficient has been developed for an electron and a hydrogen ion in an ambient molecular gas. The quasi-equilibrium equations for number densities of atoms in different levels are rewritten. The recombination coefficient flowing through every level has been calculated in comparison of the termolecular recombination coefficient defined by Bates. The power law variation over temperature of the recombination coefficients has been represented. Structureless ionic core model has been used with new approximation of radiative transition rate. New collisional rate coefficients are calculated by integrating the inelastic scattering cross sections. Based on the quantal-classical correspondence theory, the new form of quantum impulse cross section has been calculated for inelastic collision between the ionized hydrogen atom and the incoming molecular.

The incoming molecular are popular gases in the atmosphere, such as hydrogen, nitrogen, oxygen, carbon monoxide, carbon dioxide and water vapor. During the inelastic collision, the internal energy of the incoming molecular has been changed. Both of the rotational and vibrational energy change have been considered. Up-to-date data of cross section colliding with electron of these molecular have been used as the scattering amplitude. Cross sections have been integrated over the phase space ( $d\mathbf{r}d\mathbf{p}$ ) and the limits have been carefully determined and showed in details.

Cross sections of  $n \rightarrow n'$ ,  $nl \rightarrow n'l'$ , and  $nl \rightarrow n'l'$  transitions have been calculated and the relations between them have been proven by the results.

Cross sections of  $n \rightarrow n'$  transitions of hydrogen atom and rotational transitions of molecular hydrogen have been calculated and compared with the results by the binary encounter approximation theory. It is shown that the inelastic quantum impulse cross section satisfied the detail balance relation and so do the rate coefficients.

Also  $n \rightarrow n'$  transitions have been used in calculating the rate coefficients, which have

been put into the quasi-equilibrium equations to obtain the recombination coefficients. Different recombination coefficients have been obtained for different Temperatures. Rates coefficient of inelastic transitions by resonant transfer of electronic excitation have been calculated and compared to the previous classical results. The comparisons of the inelastic coefficients to the elastic results are also represented.

# CHAPTER I

## INTRODUCTION

Three-body recombination is a well-studied topic that has lasted for more than four decades. It deals with the recombination coefficient for an electron combining with an ionized atom by colliding with an incoming neutral particle, which generally is a atom or a molecule. It is a fundamental phenomenon in plasmas and it is an interesting topic in many areas. It is found it play an important role in astrophysics, interstellar chemistry, comets, shock waves, Bose-Einstein condensation, and also in Fermi gases. Especially in aeronomy, people are interested in how long will it take to eliminate the ionized track of a nose cone re-entry. The air friction ablates the surface of the space shuttle and forms a layer of plasma, which block the communication. It is very interesting to study that how would an upper atmosphere gas molecule, such as  $N_2$ ,  $O_2$ ,  $CO_2$ , and  $H_2O$ , collide with the electron, absorb the kinetic energy by rotational and vibrational excitation, and help the electron recombining with the metallic ion and neutralize the plasma.

Different theories had been used to approach the solution. In 1924, Thomson gave an early theory for the recombination rate with a simple assumption that the probability of recombining is inversely proportional to the mean free path of the electron [1]. Pitaevskii (1962) treated the problem as a diffusion process and proposed a much more advanced theory using Fokker-Planch equation [2]. Bates, Kingson and McWhirter (1962) have written a set of quasi-equilibrium equations for the number densities of the recombining atoms [3][4]. Bates and Khare (1964) calculated the recombination coefficient using the collisional conductances which in terms of the rate coefficients of the electron-atom collision that cause the electron to transit to another level [5]. In 1970, the theory had been extended to inelastic collision by Bates, Malaviya, and Young [6]. Flannery (1970) developed a binary encounter theory, which take care of the small part that Bates and his colleagues had omitted in

their assumption and made the theory satisfy the detailed balance relation [7]. In 1973 Flannery also extended this theory to the inelastic process [8]. Bates (1981) has calculated the combination coefficients with the quasi-equilibrium equations for inelastic collision [9].

In 2000, Flannery developed a new approach to the cross sections of three-body recombination, the quantum impulse approximation(QIA) [10]. Instead of using semiquantal method and treat the particles classically, he started from the transition matrix for scattering and replaced the densities by the classical distribution in the end, providing a new path consistent with the classical correspondence.

### ***1.1 Binary Encounter Approximation***

Binary encounter approximation(BEA) treats the collision as a classical procedure. It is assumed that the collision between the incoming particle and the electron happens so quickly that the nucleus is unaffected. The potential energy is unchanged. The change in total energy of the electron-ion system has the same limits as the change of kinetic energy,

$$\frac{1}{2}m_e(v_e'^2 - v_e^2) = M_{ea}\mathbf{V}_{ea} \cdot (\mathbf{g}_{ea}' - \mathbf{g}_{ea}) - \frac{M_{ea}^2}{M_e + M_i}g_{ea}^2(1 - \cos\psi). \quad (1.1)$$

Differential cross sections are integrated over the spatial angle, the kinetic energy, and the relative velocity of the electron and the incoming particle. Quantum mechanical distribution is adopted for the kinetic energy to makes the BEA method "semiquantal"

### ***1.2 Quantum Impulse Approximation***

The quantum impulse approximation method uses the quantum scattering transition Matrix  $T$  to calculate the cross section. The potential energy of the electron-ion system is ignored and the transition matrix for the free target is used. This also implies the same assumption that the nucleus left unaffected as the BEA. The transition matrix is in terms of quantal distribution  $\rho$  which can be replaced by classical distribution

$$\rho^c = \{\delta(p^2/2m + V(r) - E)dE\}\{\delta(|\mathbf{r} \times \mathbf{p}| - \mathbf{L})dL\}. \quad (1.2)$$

With the angular integration, total cross section of transition  $nl \rightarrow n'l'$  can be obtained by integrating the scattering amplitude over the phase space.

### 1.3 *Rate Coefficients and Combination Coefficients*

Rate coefficients can be obtained by integrating the cross section over the magnitude of the velocity of the incoming particle,

$$K(\mathcal{E}, \Delta_3)dE_f = dE_f \int v_3 \mathcal{G}(v_3) Q(\mathcal{E}, \Delta_3; v_3) dv_3. \quad (1.3)$$

Combination coefficient are calculated by summing all the rate coefficients that transits into several lowest energy levels where the electrons can hardly escape,

$$\alpha_3 = \frac{1}{n_e N^+} \sum_{p>u} n_E(p) \rho(p) \left( \sum_{q<r} (K(p, q) + \frac{1}{N} A(p, q)) \right). \quad (1.4)$$

### 1.4 *Detailed Balance Relation*

For the cross section for the transition of  $i$  to  $f$ , the detailed balance relation should be satisfied,

$$p_i^2 \sigma_{if} = p_f^2 \sigma_{fi}. \quad (1.5)$$

Similarly, the rate coefficients should also satisfy the detailed balance relation. With  $n^2$  degenerate levels in level  $n$ ,

$$n^2 \exp(-E_n/KT) K(n, m) = m^2 \exp(-E_m/KT) K(m, n). \quad (1.6)$$

### 1.5 *Our New Mission*

With the most recent experimental data, we are able to calculate the new cross sections obtained from quantum impulse approximation theory that was extended to the inelastic collision. New rate coefficients will be calculated and compared with the results from the binary encounter approximation. The combination coefficient should be confirmed by comparing the rate flow that pass through each level as the quasis-equilibrium is established.



## CHAPTER II

### PREVIOUS WORKS

#### 2.1 *Quasi-equilibrium Equation*

Bates, Kingston and McWhirter (1962) wrote down a set of equations of the number densities of atoms [3][4] in quasi-equilibrium for the recombination of electron with bare nuclei  $N^{Z+}$  in the collision with another electron,

$$\begin{aligned} \dot{n}(p) = & -n(p)[n(c)\mathcal{K}(p) + \mathcal{A}(p)] + n(c) \sum_{q \neq p} n(q)K(q, p) \\ & + \sum_{q > p} n(q)A(q, p) + n(c)n(N^{Z+})[K(c, p) + \beta(p)], \end{aligned} \quad (2.1)$$

where

$$\mathcal{K}(p) = K(p, c) + \sum_{q \neq p} K(p, q), \quad \mathcal{A}(p) = \sum_{q < p} A(p, q).$$

$K(p, q)$  is the rate coefficient for the transition of the atom from level  $p$  to  $q$ ,  $A(p, q)$  is the Einstein spontaneous transition probability,  $\beta(p)$  is the rate coefficient for radiative recombination.  $K(c, p)$  is the rate coefficient for the transition of a free electron combined to level  $p$  and  $n(q)$ ,  $n(c)$  and  $n(N^{Z+})$  are the number densities for the atoms at level  $p$ , the free electrons and the nuclei  $N^{Z+}$  respectively. In quasi-equilibrium, the above equations equals and the number densities will be the same as in Saha equilibrium when  $p$  reaches a certain high level.

#### 2.2 *Bates' Semi-quantal Theory*

Bates and Khare (1964) developed a semi-quantal method for the solution of three-body recombination [5]. The energetic electron was assumed to be passing through a hydrogenic level of the ion/nucleus as it collide with the incoming atom. Therefore recombination

coefficient  $\alpha$  for process



may be expressed in terms of the rate coefficient  $k(p, q)$  of the transition



The energy change of the electron is written as

$$\Delta = -m\mathbf{U} \cdot (\mathbf{V}_{e1} - \mathbf{V}_{e2}) - \frac{2m^2}{M} \mathbf{V}_e \cdot (\mathbf{V}_{e1} - \mathbf{V}_{e2}), \quad (2.4)$$

where  $\mathbf{U}$  is the velocity of the incoming particle relative to the center of mass of the ion-electron system and  $\mathbf{V}_e$  and  $\mathbf{V}_a$  are the velocities of the electron and the atom relative to the ion. Label 1 or 2 indicates that the velocity is before or after the collision.  $m$  and  $M$  are the masses of the electron and the atom, respectively.

The second term of the equation above is ignored when  $m$  is very small compare to  $M$ . The magnitude of  $\mathbf{V}_{e1}$  and  $\mathbf{V}_{e2}$  are set to be the same.

The rate coefficient  $k(p, q)$  can be obtained by integrating the product of the velocity of the electron and the cross section with above restriction over all the possible region in the phase space of the velocity. The energy change between the two level  $p$  and  $q$  is written as

$$\Delta = E_0(1/p^2 - 1/q^2), \quad (2.5)$$

where  $E_0$  is the ionization potential of hydrogen.

The recombination coefficient can be estimated with the formula

$$\alpha = \left(\frac{h^2}{2\pi m k \theta}\right)^{3/2} \left(\sum_q \frac{1}{\mathcal{C}(q)}\right)^{-1}, \quad (2.6)$$

where  $\theta$  is the temperature,

$$\mathcal{C}(q) = N \sum_{s=0}^{\infty} \sum_t (1+s+t)(q+s)^2 k(q+s, q-1-t) \exp^{-\epsilon(q+s)}, \quad (2.7)$$

and  $N$  is the number density of the atoms.

This theory was later applied to the process in a molecular gas  $Z$  by Bates and Malaviya [6]. The collision is considered inelastic and the internal energy of  $Z$  is changed through the rotational or vibrational transitions. The recombination coefficient  $\alpha$  of the process



may be expressed in terms of the rate coefficient  $k(n, m)$  of the transition

$$X(n) + Z \rightarrow X(m) + Z. \quad (2.9)$$

The energy change of the electron is written as

$$\Delta = -I - m\mathbf{U} \cdot (\mathbf{V}_{\mathbf{e1}} - \mathbf{V}_{\mathbf{e2}}) - \frac{m^2}{M} \mathbf{V}_{\mathbf{e1}} \cdot (\mathbf{V}_{\mathbf{e1}} - \mathbf{V}_{\mathbf{e2}}), \quad (2.10)$$

where  $I$  is the increased internal energy of the molecule.  $M$ ,  $m$ ,  $\mathbf{U}$ ,  $\mathbf{V}_{\mathbf{e1}}$  and  $\mathbf{V}_{\mathbf{e2}}$  are defined as before. Again the last term is ignored. The rate coefficient was to averaging over the initial rotational or vibrational levels  $i$  and sum over the final levels  $j$ . It also contains the elastic rate coefficient  $k_0(n, m)$  as Bates and Khare calculated before ( $k(p, q)$ ) [5],

$$k(n, m) = k_0(n, m) + k_x(n, m), \quad (2.11)$$

where

$$k_x(n, m) = \frac{1}{f_Z(\theta)} \sum_i \sum_{j \neq i} \omega_i \exp(-\epsilon_i) k(n, m|i, j), \quad (2.12)$$

$f_Z(\theta)$  is the partition function for the internal degrees of freedom of the molecule,  $\omega_i$  is the statistical weight of the molecular internal energy level  $i$  and  $k(n, m|i, j)$  is the rate coefficient as the internal energy of the molecular changes from level  $i$  to level  $j$ .

The total combination coefficient can be obtained by

$$\alpha = \left(\frac{h^2}{2\pi m k \theta}\right)^{3/2} \left(\sum_q \frac{\mu(q)}{\mathcal{C}(q) + \mathcal{A}(q)}\right)^{-1} + \alpha_R, \quad (2.13)$$

where  $\alpha_R$  is the radiative recombination coefficient

$$\mu = \frac{\mathcal{C}(q+1)/\mathcal{A}(q+1)}{1 + \mathcal{C}(q+1)/\mathcal{A}(q+1)}, \quad (2.14)$$

$$\mathcal{A}(q) = q^2 A(q) \exp(\epsilon(q)), \quad (2.15)$$

where  $A(q)$  is the sum of the spontaneous transition probabilities from level  $q$  to all lower levels excluding the ground level.

In 1981, Bates developed a different approach to the collisional recombination coefficient [9].

$$\alpha_3 = \frac{1}{n(e)^2} \sum_{q>r} n_E(q) \rho(q) \left[ \sum_{u<r} (k(q, u) + \frac{1}{N} A(q, u)) \right], \quad (2.16)$$

where  $n(e)$  is the electron density,  $n_E(q)$  is the number density in level  $q$  in thermodynamic equilibrium, and  $A(q, u)$  is the Einstein spontaneous transition probability.  $\rho$  is defined as

$$\rho(p) = n(p)/n_E(p), \quad (2.17)$$

where for  $u < r$ ,  $\rho(u)$  is close to zero.  $\rho$  satisfies the quasi-equilibrium equations

$$\rho(p)\mathcal{K}(p) = \sum_{m \neq p, \leq s} \rho(m)(k(p, m) + \frac{n_E(m)}{n_E(p)N}A(m, p)) + K(p, \sigma) + K(p, c), \quad (2.18)$$

where  $n_E(p)$  is the number density in thermodynamic equilibrium and for  $p > s$ ,  $\rho(p)$  is close to unity.  $K(p, c)$  is the ionizing rate coefficient.

$$\mathcal{K}(p) = K(p, c) + \sum_{m \neq p} K(p, m) + \frac{1}{N} \sum_{m < p, \neq 1, 2} A(p, m), \quad (2.19)$$

and

$$K(p, \sigma) = \sum_{m > s} K(p, m). \quad (2.20)$$

### 2.3 *Flannery's Binary Encounter Approximation*

Flannery (1972) formulated a new form of rate coefficient  $k(n, m)$  [8] for the three-body ionic recombination process



with an exact expression of the change for energy of the electron contrasting the previous classical assumption, which neglected a small part of the energy change as the mass difference is large. For elastic collision with incoming atom, the energy change takes the form:

$$\frac{1}{2}M_1(v_1'^2 - v_1^2) = M_{13}\mathbf{V}_{13} \cdot (\mathbf{g}_{13}' - \mathbf{g}_{13}), \quad (2.22)$$

where  $M_1$  and  $v_1$  are the mass and velocity of the electron.  $M_{13}$  and  $\mathbf{V}_{13}$  is the reduced mass and center-of-mass velocity of the ion and the incoming atom.  $\mathbf{g}_{13}$  is the relative velocity of the electron to the incoming atom. Vectors with prime are the corresponding vectors

after collision. The reference frame is chosen so that the center of mass of the ion-electron system is initially at rest. The energy change of the electron-ion system is

$$\frac{1}{2}M_{12}(v_{12}'^2 - v_{12}^2) = M_{13}\mathbf{V}_{13} \cdot (\mathbf{g}_{13}' - \mathbf{g}_{13}) - \frac{M_{13}^2}{M_1 + M_2}g_{13}^2(1 - \cos \psi), \quad (2.23)$$

where  $M_2$  is the mass of the ion and  $\psi$  is the angle that  $g_{13}$  rotated during the collision. The magnitude of  $\mathbf{g}_{13}$ ,  $g$ , is not changed.  $\mathbf{g}_{13}^{(')}$  are set to have angles  $\eta^{(')}$  with  $V_{13}$ , which is not changed. The plane that contains  $\mathbf{V}_{13}$  and  $\mathbf{g}_{13}$  has an angle of  $\phi$  with the plane that contains  $\mathbf{g}_{13}^{(')}$ . The energy difference can be expressed by

$$E_f - E_i = M_{13}V_{13} \sin \eta \sin \psi \cos \phi - \frac{M_{13}^2}{M_1 + M_2}g^2 + M_{13}V_{13} \cos \eta(1 - \cos \psi). \quad (2.24)$$

When the incoming third-body is a molecule, the collision can be inelastic and the internal energy of the molecule can increase an amount of  $\Delta_3$  through rotational or vibrational transitions. With the same setting, the energy change of the electron-ion system is

$$\mathcal{E} = E_f - E_i = M_{13}V_{13}(g' \cos \eta' - g \cos \eta) + \frac{M_{13}^2}{M_1 + M_2}(gg' \cos \psi - g^2) - \frac{a}{1 + a}\Delta_3, \quad (2.25)$$

where  $g'$  is the magnitude of  $\mathbf{g}_{13}'$  and is different from  $g$ , and

$$a = \frac{M_2M_3}{M_1(M_1 + M_2 + M_3)}. \quad (2.26)$$

With this restriction, the rate coefficient can be obtained by integrating the product of velocity and the cross section over the phase space,

$$K(\mathcal{E}, \Delta_3)dE_f = dE_f \int v_3 \mathcal{G}(v_3) Q(\mathcal{E}, \Delta_3; v_3) dv_3, \quad (2.27)$$

where  $\mathcal{G}$  is the velocity distribution of the third body that has velocity  $v_3$  and  $Q(\mathcal{E}, \Delta_3; v_3)$  is the cross section that

$$Q(\mathcal{E}, \Delta_3; v_3)dE_f = \frac{dE_f}{v_3^2} \int \frac{\mathcal{F}(v_1)}{v_1} dv_1 \int \frac{g^2 dg}{\omega \gamma(v_1, v_2, g)} \int \frac{\sigma_{13} d \cos \psi}{[(\cos \psi^+ - \cos \psi)(\cos \psi^- - \cos \psi^-)]^{1/2}}, \quad (2.28)$$

where  $\mathcal{F}$  is the velocity distribution of electron,  $\psi^{+(-)}$  are the limits of  $\psi$ ,  $\sigma_{13}$  is the differential cross section for electron-atom collision, and

$$\omega = g'/g, \quad (2.29)$$

$$\gamma^2 = \frac{M_{13}^2 g^2}{(1 + a)^2} [(1 + a)(v_1^2 + av_3^2) - ag^2]. \quad (2.30)$$

## 2.4 Flannery's Quantum Impulse Approximation

The quantum impulse approximation assumes that the interaction between the incoming particle  $i$  and the electron  $j$  is fast enough so that the third particle  $k$  remains unaffected [10]. The quantum differential cross section can be expressed by the transition matrix  $T_{if}(\mathbf{p}_i, \mathbf{p}'_i)$

$$\frac{d\sigma_{if}}{d\hat{\mathbf{p}}'_i} = \frac{v'_i}{v_i} \left( \frac{1}{4\pi} \frac{2\mathcal{M}_i}{\hbar^2} \right) \|T_{if}(\mathbf{p}_i, \mathbf{p}'_i)\|^2, \quad (2.31)$$

where  $\mathcal{M}_i$  is the effective mass of incoming particle and electron-ion system,  $\mathbf{p}_i^{(')}$  are the momenta of the incoming particle before and after the collision, and  $v_i^{(')}$  are the corresponding velocities. The reference frame is chosen as the initial electron-ion center of mass frame. The transition matrix is expressed in terms of the probability density  $\rho(\mathbf{r}, \mathbf{p})$

$$\|T_{if}(\mathbf{p}_i, \mathbf{p}'_i)\|^2 = (2\pi\hbar)^3 \int d\mathbf{p} \int d\mathbf{r} \rho_f * (\mathbf{r}, \mathbf{p} + \mathbf{q}) \times \|T_{ij}\|^2 \rho_f * (\mathbf{r}, \mathbf{p} + \mathbf{q}), \quad (2.32)$$

where  $p, r$  are momentum and displacement in the electron-ion center of mass frame and

$$q = p' - p. \quad (2.33)$$

The two-body transition matrix  $T_{ij}$  can be expressed by scattering amplitude  $f_{ij}$ . The quantal distribution can be substituted by the corresponding classical phase-space distribution

$$\rho^c = \{\delta(p^2/2m + V(r) - E)dE\}\{\delta(\|\mathbf{r} \times \mathbf{p}\| - L)dL\}, \quad (2.34)$$

which depends on the angular momentum.  $m$  is the electron mass in the electron-ion center of mass frame. The degenerate levels no longer have the same probability and the total cross section of transition  $nl \rightarrow n'l'$  can be determined with a new restriction on angular momentum,

$$m^2(\dot{r} \pm \dot{r}')^2 + (L - L')^2/r^2 \leq q^2 \leq m^2(\dot{r} \pm \dot{r}')^2 + (L + L')^2/r^2. \quad (2.35)$$

By summing over the initial  $l$  states and the final  $l'$  states, the total cross section of transition  $nl \rightarrow n'$  and  $n \rightarrow n'$  can also be obtained by integrating over the phase space of

$(\hat{p}'_i, \mathbf{p}, \mathbf{r})$ . A general expression of the total cross section  $\sigma(\mathbf{p}_i)$

$$\sigma(\mathbf{p}_i) = \frac{2\pi}{M_{ij}^2 v_i^2} \int q dq \int P(r, q) dr \frac{1}{\pi} \int \frac{\|f_{ij}(g, q)\|^2 dg^2}{(g^2 - g_-^2)(g_+^2 - g^2)^{1/2}}, \quad (2.36)$$

where  $M_{ij}$  is the effective mass of the electron and the incoming particle,  $g$  is the relative velocity magnitude with the limits  $g_-$  and  $g_+$ , and  $P(r, q)$  is the classical probability that are different for different transition.

## CHAPTER III

### COLLISIONS AND THE BASIC SET UP

An electron can combine with an ion or nucleus in different ways. In tenuous plasmas, it happens with radiation. If the plasmas is dense, it can happen in the collision with a third particle. The collision can be elastic, where the third particle takes away the kinetic energy. The collision can also be inelastic, where the third particle is excited to a higher internal energy level. At a relatively low temperature (thermal energy smaller than  $1eV$ , we consider the case with temperature  $< 5000K$ ), the thermal kinetic energy the electron has is generally not enough to excite the electrical energy level. But it is enough to excite the rotational and vibrational energy levels of some molecules, such as  $CO_2$  and  $H_2O$ . It is important to include the inelastic collisional recombination coefficients due to these transitions.

The recombination coefficient is defined in the equation of the change of the number density of the combined atom

$$\frac{dn(X)}{dt} = \alpha n(e)n(X^+) - k_d n(X), \quad (3.1)$$

where  $k_d$  denotes the dissociate coefficient,  $n(X^+)$  is the number density of the ion,  $n(e)$  is the number density of free electrons, and  $n(X)$  is the number density of the combined atom. To get the recombination coefficient, we must consider all the recombining and dissociating processes. A free electron can get into bounded level after colliding with a third particle. An atom can be ionized in the reverse procedure. An electron can also jump to another level via collision or radiation. Following the set up in [3]. Let  $K(p, m)$  be the rate coefficient for the process





$K(p, c)$  be the rate coefficient for the process



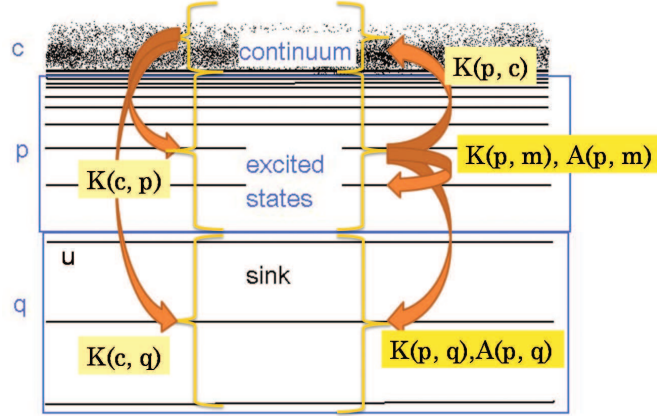
$K(c, p)$  be the rate coefficient for the process



$\beta(p)$  be the rate coefficient for radiative recombination



and  $A(p, m)$  be the spontaneous transition probability for



**Figure 3.1:** Transitions between energy levels

All those different processes are happening simultaneously in the plasmas. As the recombination happens, electrons start to fall into those excited states,  $m's$ , and eventually stay on those lower energy levels ( $q < u$ ), labeled as “sink” in figure 3.1, which have larger energy gaps and “trap” electrons in them.  $u$  denotes the level as the boundary of the sink. The number densities of electrons and ions are considered much larger then the number densities of the excited atoms,  $n(p)$ . Therefore the processes can immediately reach a

quasi-equilibrium condition that the rates of input transitions of level  $p$  equal to the rates of output transitions. So the number density  $n(p)$  can be considered not changing. Write  $N$  for the number density of the molecular gas. The rate of increase of  $n(p)$  with time  $t$  is given by

$$\begin{aligned}\dot{n}(p) = & -n(p)[N(K(p, c) + \sum_{m \neq p} K(p, m)) + \sum_{m < p} A(p, m)] \\ & + N \sum_{m \neq p} n(m)K(m, p) + \sum_{m \neq p} n(m)A(m, p) \\ & + n(X^+)n(e)NK(c, p) + n(X^+)n(e)\beta(p),\end{aligned}\tag{3.7}$$

which is similar to equation (6) in [3]. Define

$$\rho(p) = n(p)/n_E(p),\tag{3.8}$$

where  $n_E(p)$  is the corresponding number density in Saha equilibrium (thermodynamic equilibrium), which describes the degree of ionization of plasmas in certain temperature, density, and ionization energies of the atoms. We have the well known formula for Saha equilibrium (Fowler 1936) [11]

$$\frac{n_E(p)}{n(e)n(X^+)} = p^2 \left( \frac{h^2}{2\pi m_e kT} \right)^{3/2} \exp(I_p/kT),\tag{3.9}$$

where  $I_p$  is the ionization energy of level  $p$ . Also, from the principle of the detailed balancing, we know that

$$n_E(m)K(m, p) = n_E(p)K(p, m),\tag{3.10}$$

$$n(X^+)n(e)K(c, p) = n_E(p)K(p, c).\tag{3.11}$$

Therefore, for a quasi-equilibrium system, The derivative in equation (3.7) can be set to zero. Divide both sides of the equation (3.7) by  $Nn_E(p)$  and we can get

$$\begin{aligned}\rho(p)[(K(p, c) + \sum_{m \neq p} K(p, m)) + \frac{1}{N} \sum_{m < p} A(p, m)] = \\ \sum_{m \neq p} \rho(m)(K(p, m) + \frac{n_E(m)}{n_E(p)N} A(m, p)) \\ + K(p, c) + \frac{n(e)n(X^+)}{Nn_E(p)} \beta(p),\end{aligned}\tag{3.12}$$

which gives us the distribution of number densities  $n(p)$ . The last term of radiative recombination can be ignored since it is really small compared to other rates. From (3.9), (3.10) and (3.11), we can obtain

$$\frac{n_E(p)}{n(e)n(X^+)} = 4.2 \times 10^{-16} \frac{p^2}{T^{3/2}} \exp\left(\frac{157890}{p^2 T}\right) \text{ cm}^3, \quad (3.13)$$

$$\frac{n_E(m)}{n_E(p)} = \frac{m^2}{p^2} \exp\left(157890 \frac{p^2 - m^2}{m^2 p^2 T}\right). \quad (3.14)$$

Thus the equation (3.12) can be expressed as

$$\begin{aligned} \rho(p)[(K(p, c) + \sum_{m \neq p} K(p, m)) + \frac{1}{N} \sum_{m < p} A(p, m)] = \\ + \sum_{q \neq p < s} \rho(m) \left( K(p, m) + \frac{m^2}{N p^2} \exp\left(157890 \frac{p^2 - m^2}{m^2 p^2 T}\right) A(m, p) \right) + K(p, c). \end{aligned} \quad (3.15)$$

With these number densities and rate coefficients, we can obtain the rates for all the transitions that go into the sink. So the three-body recombination coefficient,  $\alpha_3$ , can be obtained from

$$\alpha_3 = \frac{1}{n(e)n(X^+)} \sum_{p > u} n_E(p) \rho(p) \sum_{q < u} \left( K(p, q) + \frac{1}{N} A(p, q) \right), \quad (3.16)$$

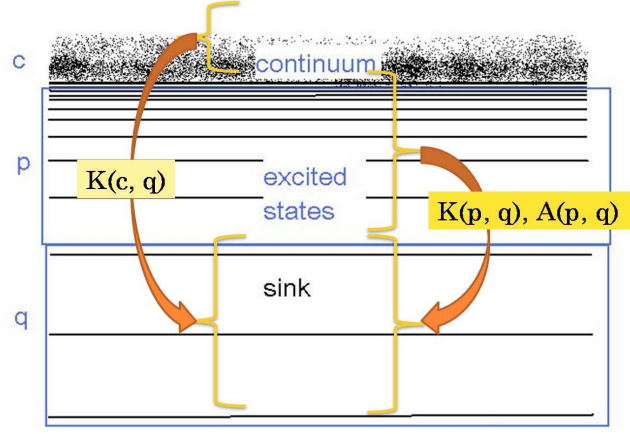
which sums over all the transitions that go into the levels in the sink ( $q < u$ ) and direct transitions from the continuum to the sink is ignored. With (3.13),  $\alpha_3$  can be written as

$$\alpha_3 = \frac{4.2 \times 10^{-16}}{T^{3/2}} \sum_{p > u} p^2 \exp\left(\frac{157890}{p^2 T}\right) \rho(p) \sum_{q < u} \left( K(p, q) + \frac{1}{N} A(p, q) \right). \quad (3.17)$$

Once electrons enter the sink, they will be “trapped” in there and complete the procedure of “recombination” (figure 3.2).

### 3.1 Basic Setup

Following Flannery’s quantum impulse approximation [10], a similar expression for cross section can be applied to the inelastic collision, in which the incoming particle is no longer an atom or electron, but a molecule. The energy gaps of the rotational and the vibrational energy levels of molecules are small enough to be excited during the collision. The kinetic energy and the relative velocity between the electron and the molecule are changed after



**Figure 3.2:** Transitions of recombination

collision. Nonetheless, as we show in this chapter, the cross section takes the same form although the limits are different.

The ionized atom, left with an ion and an electron, which can be considered hydrogenic. The electron, labeled  $j$ , is energetic and is assumed to be passing through a certain hydrogenic state. The incoming third body, labeled  $i$ , which is a molecule, therefore has a better chance to collide with this electron than with the ion. In the collision with the electron, the incoming molecule changes its velocity immediately and possibly changes the internal energy via rotational or vibrational transition. The ion/nucleus, labeled  $k$ , maintains the same velocity after the collision in the initial center-of-mass frame of the electron-ion system ( $CM(j, k)$ ). ( $CM(j, k)$  frame will be used throughout this article.)

The masses are labeled  $m_i$ ,  $m_j$  and  $m_k$  for the particle  $i$ ,  $j$  and  $k$ , respectively.  $M_{ij}$  and  $m$  are set to be the reduced masses of the center-of-mass of the  $(i, j)$  system and the  $(j, k)$  system.  $M$  is the total mass and  $\mu_i$  is the reduced masses of the center-of-mass of  $i - (jk)$  system

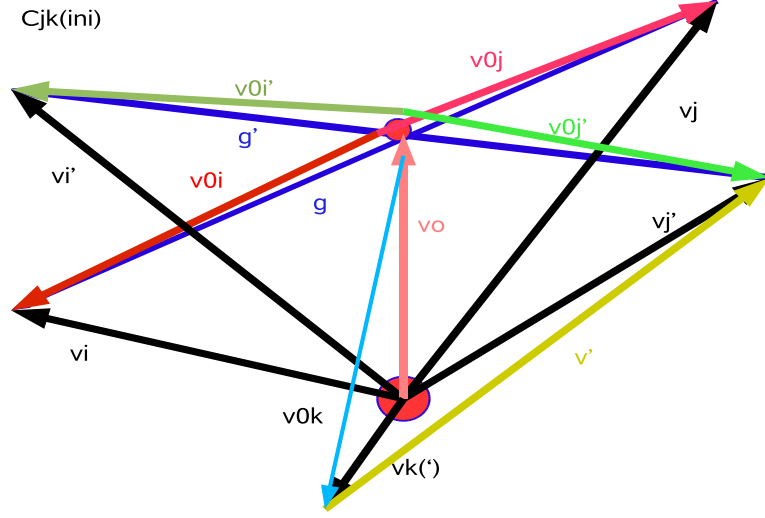
$$M_{ij} = \frac{m_i m_j}{m_i + m_j}, \quad (3.18)$$

$$m = \frac{m_j m_k}{m_j + m_k}, \quad (3.19)$$

$$M = m_i + m_j + m_k, \quad (3.20)$$

$$\mu_i = \frac{m_i (m_j + m_k)}{m_i + m_j + m_k}. \quad (3.21)$$

The definitions of velocities of the three particles are shown in figure 3.3.  $\mathbf{v}_i^{(')}$ ,  $\mathbf{v}_j^{(')}$  and



**Figure 3.3:** Definitions of velocities.

$\mathbf{v}_k^{(')}$  are velocities of particle  $i$ ,  $j$  and  $k$ . After the collision, the velocities are labeled with primes.  $\mathbf{v}_{0i}^{(')}$ ,  $\mathbf{v}_{0j}^{(')}$  and  $\mathbf{v}_{0k}^{(')}$  are velocities of particle  $i$ ,  $j$  and  $k$  relative to the center-of-mass of  $(i, j)$  system.  $\mathbf{g}^{(')}$  are relative velocities between  $i$  and  $j$ .

The velocity of the center-of-mass of  $(i, j)$  system,  $\mathbf{v}_0$ , stays the same after the collision. So does the velocity of particle  $k$ ,  $\mathbf{v}_k$ . Let  $\mathbf{v}_{0k}$  be the relative velocity of the center-of-mass of  $(i, j)$  system to particle  $k$ . Let  $\mathbf{v}^{(')}$  be the relative velocities of particle  $j$  to particle  $k$ , before and after the collision. We have the following relations

$$\mathbf{g}^{(')} = \mathbf{v}_i^{(')} - \mathbf{v}_j^{(')} = \mathbf{v}_{0i}^{(')} - \mathbf{v}_{0j}^{(')}, \quad (3.22)$$

$$\mathbf{v}_{0k} = \mathbf{v}_k - \mathbf{v}_0, \quad (3.23)$$

$$\mathbf{v}^{(')} = \mathbf{v}_j^{(')} - \mathbf{v}_k = \mathbf{v}_{0j}^{(')} - \mathbf{v}_{0k}. \quad (3.24)$$

The definitions of vectors  $\mathbf{g}^{(')}$  are in the opposite direction of  $\mathbf{g}^{(')}$  defined by Flannery (1970) [7].

### 3.2 Momentum Conservation

Momentum is conserved during the collision. In the reference frame of the center-of-mass of the  $(i, j)$  system, the sum of the momenta of two particles is zero.

$$\mathbf{p}_{0i} + \mathbf{p}_{0j} = \mathbf{p}'_{0i} + \mathbf{p}'_{0j} = 0, \quad (3.25)$$

and in the reference frame of the initial center-of-mass of  $(j, k)$  system,

$$\mathbf{p}_i + \mathbf{p}_j = \mathbf{p}'_i + \mathbf{p}'_j, \quad (3.26)$$

where  $\mathbf{p}_i^{(')}$  and  $\mathbf{p}_j^{(')}$  are the momenta of particle  $i$  and  $j$ , primes indicate the momenta after the collision,

$$\mathbf{p}_{0i}^{(')} = m_i \mathbf{v}_{0i}^{(')}, \quad (3.27)$$

$$\mathbf{p}_{0j}^{(')} = m_j \mathbf{v}_{0j}^{(')}, \quad (3.28)$$

$$\mathbf{p}_i^{(')} = m_i \mathbf{v}_i^{(')}, \quad (3.29)$$

and

$$\mathbf{p}_j^{(')} = m_j \mathbf{v}_j^{(')}. \quad (3.30)$$

Since

$$\mathbf{v}_{0i}^{(')} = \frac{m_j}{m_i + m_j} \mathbf{g}^{(')}, \quad \mathbf{v}_{0j}^{(')} = -\frac{m_i}{m_i + m_j} \mathbf{g}^{(')}, \quad (3.31)$$

we have the expression of  $v_0$ , the relative velocity between the two frames that discussed above,

$$\mathbf{v}_0 = \mathbf{v}_i - \mathbf{v}_{0i} = \mathbf{v}_i - \frac{m_j}{m_i + m_j} \mathbf{g} = \frac{m_i \mathbf{v}_i}{m_i + m_j} + \frac{m_j \mathbf{v}_j}{m_i + m_j} = \frac{\mathbf{p}_i + \mathbf{p}_j}{m_i + m_j}. \quad (3.32)$$

Define  $q_j$  as the difference of the momenta in the  $(j, k)$  center-of-mass frame,

$$\mathbf{q}_j = \mathbf{p}_i - \mathbf{p}'_i = \mathbf{p}'_j - \mathbf{p}_j, \quad (3.33)$$

and let  $\mathbf{p}^{(')}$  be the relative momenta of  $j$  to  $k$ , before and after the collision,

$$\mathbf{p}^{(')} = m \mathbf{v}^{(')}, \quad (3.34)$$

and define  $q$  as the change of relative momentum of  $j$  to  $k$ ,

$$\mathbf{q} = \mathbf{p}' - \mathbf{p} = m(\mathbf{v}' - \mathbf{v}), \quad (3.35)$$

those two "change of momenta" are deferred by a factor of  $m/m_j$ . When  $m_j \ll m_k$ , they can be considered equal,

$$\mathbf{q} = \frac{m}{m_j} \mathbf{q}_j = \frac{m_k}{m_j + m_k} \mathbf{q}_j. \quad (3.36)$$

Define the relative momenta of  $i$  and  $j$  in the  $(i, j)$  center-of-mass frame as

$$\mathbf{p}_{ij}^{(\prime)} = M_{ij} \mathbf{g}^{(\prime)}. \quad (3.37)$$

We have

$$|\mathbf{p}_{ij}^{(\prime)}| = |\mathbf{p}_{0i}^{(\prime)}| = |\mathbf{p}_{0j}^{(\prime)}|. \quad (3.38)$$

The change of momentum  $q_j$  can also be expressed as

$$\mathbf{q}_j = \mathbf{p}_{ij} - \mathbf{p}_{ij}' = M_{ij}(\mathbf{g} - \mathbf{g}'). \quad (3.39)$$

### 3.3 *Change of the Total Kinetic Energy*

The kinetic energy lost by the electron in the inelastic collision is defined as  $\Delta$ , in the electron-molecule,  $(j, k)$ , center-of-mass frame. The lost is compensated for by the increase of the internal energy of the incoming molecule and the electron falls onto another level after the collision,

$$\frac{1}{2} m_i \mathbf{v}_{0i}^2 + \frac{1}{2} m_j \mathbf{v}_{0j}^2 = \frac{1}{2} m_i \mathbf{v}_{0i}'^2 + \frac{1}{2} m_j \mathbf{v}_{0j}'^2 + \Delta. \quad (3.40)$$

Writing

$$\mathbf{v}_{0i}^{(\prime)} = -\frac{m_j}{m_i} \mathbf{v}_{0j}^{(\prime)}, \quad \mathbf{v}_{0j}^{(\prime)} = -\frac{m_i}{m_j} \mathbf{v}_{0i}^{(\prime)}, \quad (3.41)$$

we reach the relation between  $\Delta$  and the changes of energy of each of the particles,

$$\Delta = \frac{m_i + m_j}{m_j} (KE_{0i} - KE_{0i}') = \frac{m_i + m_j}{m_i} (KE_{0j} - KE_{0j}'), \quad (3.42)$$

where

$$KE_{0i}^{(\prime)} = \frac{1}{2} m_i \mathbf{v}_{0i}^{(\prime)2}, \quad \text{and} \quad KE_{0j}^{(\prime)} = \frac{1}{2} m_j \mathbf{v}_{0j}^{(\prime)2}. \quad (3.43)$$

Since  $m_j \ll m_i$ , most of the lost kinetic energy are lost by the electron. Also,  $\Delta$  can be expressed with relative momenta and velocities

$$\Delta = \frac{\mathbf{p}_{ij}^2 - \mathbf{p}_{ij}'^2}{2M_{ij}} = \frac{1}{2} M_{ij} (\mathbf{g}^2 - \mathbf{g}'^2). \quad (3.44)$$

In the frame of the center-of-mass of the  $(j, k)$  system, the equation of energy conservation is

$$\frac{1}{2}m_i\mathbf{v}_i^2 + \frac{1}{2}m_i\mathbf{v}_j^2 = \frac{1}{2}m_i\mathbf{v}_i'^2 + \frac{1}{2}m_j\mathbf{v}_j'^2 + \Delta. \quad (3.45)$$

We can write the change of kinetic energy of particle  $j$  as

$$\begin{aligned} \frac{1}{2}m_j(\mathbf{v}_j'^2 - \mathbf{v}_j^2) &= \frac{1}{2}m_j((\mathbf{v}_0 - \frac{m_i}{m_i + m_j}\mathbf{g}')^2 - (\mathbf{v}_0 - \frac{m_i}{m_i + m_j}\mathbf{g})^2) \\ &= \mathbf{v}_0 \cdot M_{ij}(\mathbf{g} - \mathbf{g}') - \frac{m_i}{m_i + m_j}\Delta. \end{aligned} \quad (3.46)$$

This is the same as the equation (17) in Flannery 1973 [8]. Note that the signs  $\mathbf{g}$  and  $\mathbf{g}'$  are defined differently.

The change in the energy of  $(j, k)$  system is defined as

$$\mathcal{E} = E' - E = \frac{I}{2n} - \frac{I}{2n'}, \quad (3.47)$$

where  $I$  is the ionization potential of hydrogen. Since it was assumed the collision happened so quickly that only the particle  $i$  and  $j$  are involved and the potential energy is not changed, in the classical treatment perspective, the energy change  $\mathcal{E}$  can be expressed as the change of the kinetic energy,

$$\begin{aligned} \mathcal{E} &= \frac{1}{2}m(\mathbf{v}'^2 - \mathbf{v}^2) \\ &= \frac{1}{2}m((\mathbf{v}'_{0j} - \mathbf{v}_{0k})^2 - (\mathbf{v}_{0j} - \mathbf{v}_{0k})^2) \\ &= \frac{1}{2}m(\mathbf{v}_{0j}'^2 - \mathbf{v}_{0j}^2) - m(\mathbf{v}'_{0j} - \mathbf{v}_{0j}) \cdot \mathbf{v}_{0k} \\ &= -\frac{m}{m_j} \frac{m_i}{m_i + m_j} \Delta - \mathbf{q} \cdot \mathbf{v}_{0k}. \end{aligned} \quad (3.48)$$

So we have

$$\mathcal{E} = -\mathbf{v}_{0k} \cdot \mathbf{q} - \frac{m_k m_i}{(m_i + m_j)(m_j + m_k)} \Delta. \quad (3.49)$$

In [8], the change of energy has the expression

$$\mathcal{E} = M_{ij}\mathbf{v}_0 \cdot (\mathbf{g} - \mathbf{g}') + \frac{M_{ij}^2}{m_j + m_k} \mathbf{g} \cdot (\mathbf{g}' - \mathbf{g}) - \frac{m_k m_i}{(m_i + m_j)(m_j + m_k)} \Delta, \quad (3.50)$$



which is equivalent to (3.49). Since

$$\mathbf{v}_0 = \frac{\mathbf{p}_i + \mathbf{p}_j}{m_i + m_j}, \quad (3.51)$$

$$M_{ij}(\mathbf{g} - \mathbf{g}') = \mathbf{q}_j = \frac{m_j + m_k}{m_k} \mathbf{q}, \quad (3.52)$$

$$M_{ij}\mathbf{g} = \frac{m_j\mathbf{p}_i}{m_i + m_j} - \frac{m_i\mathbf{p}_j}{m_i + m_j}, \quad (3.53)$$

and (3.50) can be written as

$$\mathcal{E} = \frac{\mathbf{p}_i + \mathbf{p}_j}{m_i + m_j} \cdot \mathbf{q} + \frac{\mathbf{p}_j}{m_k} \cdot \mathbf{q} - \frac{m_k m_i}{(m_i + m_j)(m_j + m_k)} \Delta, \quad (3.54)$$

where the first two terms equal to the first term in (3.49)

$$\left( \frac{\mathbf{p}_i + \mathbf{p}_j}{m_i + m_j} + \frac{\mathbf{p}_j}{m_k} \right) \cdot \mathbf{q} = (\mathbf{v}_0 - \mathbf{v}_k) \cdot \mathbf{q} = -\mathbf{v}_{0k} \cdot \mathbf{q}, \quad (3.55)$$

and  $\mathbf{v}_{0k}$  is the relative velocity of the ion  $k$  to the center-of-mass of  $(i, j)$  system. It relates the two reference frames where  $g^{(')}$  and  $v^{(')}$  are defined. The kinetic energies  $M_{ij}g^{(')2}/2$  are defined in the frame of the  $(i, j)$  center-of-mass frame where  $v^{(')}$  are defined to the ion  $k$ . The relative velocity  $g^{(')}$  are not so obvious and on the contrary  $v^{(')}$  are directly related to the electron states. So for given states  $n$  and  $n'$ , which uniquely define the  $\mathcal{E}$ , with  $\mathbf{q}$  and  $\mathbf{r}$  fixed,  $\mathbf{v}_{0k}$  still remain unsure, and  $\Delta$  can still vary in a range that need to be determined.

### 3.4 Flannery's Elastic Cross Sections

The total elastic cross section of three-body recombination has been given by Flannery (2000) [10]. As we re-derived it for the inelastic collision, following the derivation in [10], [12], and [13], we find out that the inelastic cross section could have the same form. What changed is the energy lost, and  $g'$  will have a different magnitude from  $g$ . So the ranges in which  $q$ ,  $r$ ,  $p$ , and  $g$  are varying should have new limits. We will show the re-derivation below and discuss the new limits in the next chapter.

#### 3.4.1 Re-derive the Form for Cross Section

The transition frequency for the collision

$$A(\alpha) + B(\beta) \rightarrow A(\alpha') + B(\beta'), \quad (3.56)$$

is

$$\frac{dW_{if}}{dp_f} = \frac{2\pi}{\hbar} \frac{1}{g_i} \sum_{if} |V_{fi}|^2 \rho_f(E_f). \quad (3.57)$$

The QIA differential cross section of three-body-recombination has been given by Flannery (2000) [10]

$$\frac{d\sigma_{if}^{(ij)}}{d\hat{p}'_i} = \frac{v'_i}{v_i} \left( \frac{1}{4\pi} \frac{2\mu_i}{\hbar^2} \right) |T_{if}^{(ij)}|^2, \quad (3.58)$$

where the  $\hat{p}'_i$  is the scattering solid angle,

$$d\hat{p}'_i = d(\cos \psi_i) d\phi_i, \quad (3.59)$$

with  $\cos \psi_i = \hat{p}_i \cdot \hat{p}'_i$ . So

$$d(\cos \psi_i) = -\frac{q_j dq_j}{2\mu_i^2 v_i v'_i}. \quad (3.60)$$

The integration over  $d\phi_i$  is  $2\pi$ . The total cross section can be expressed as

$$\sigma_{if}^{(ij)}(p_i) = \frac{2\pi(2\pi\hbar)^3}{M_{ij}^2 v_i^2} \int q_j dq_j \int d\mathbf{r} d\mathbf{p} \rho_f * (\mathbf{p}', \mathbf{r}) |f_{ij}|^2 \rho_i(\mathbf{p}, \mathbf{r}), \quad (3.61)$$

where  $\rho_i$  and  $\rho_f$  are the probability densities before and after the collision.  $f_{ij}$  is the scattering amplitude. In [10], the probability densities were substitute by the classical phase-space distribution

$$\rho_i^c = \left\{ \frac{p^2}{2m} + V(r) - E \right\} \delta(|\mathbf{r} \times \mathbf{p}| - \mathbf{L}) dL, \quad (3.62)$$

and

$$\rho_f^c = \left\{ \frac{(\mathbf{p} + \mathbf{q})^2}{2m} + V(r) - E' \right\} \delta(|\mathbf{r} \times (\mathbf{p} + \mathbf{q})| - \mathbf{L}') dL'. \quad (3.63)$$

There are three cases of transactions:  $n \rightarrow n'$ ,  $nl \rightarrow n'$ , and  $nl \rightarrow n'l'$ . When the angular quantum number,  $l$  or  $l'$ , is specifically indicated, the angular momentum is applied.

(a)  $n \rightarrow n'$

$$\begin{aligned} \sigma_{if}^{(ij)}(p_i) &= \frac{2\pi}{v_i^2 M_{ij}^2 (2\pi\hbar)^3} \int q_j dq_j \int d\mathbf{p} dE dL dE' dL' \delta\left(\frac{p^2}{2m} + V(r) - E\right) \\ &\quad \delta\left(\frac{(\mathbf{p} + \mathbf{q})^2}{2m} + V(r) - E'\right) |f_{ij}|^2 \int r^2 d\mathbf{r} \int d\cos\theta_r \int d\phi_r, \end{aligned} \quad (3.64)$$

where  $\theta_r$  and  $\phi_r$  are the zenith and azimuth angles of  $\mathbf{r}$  to  $\mathbf{p}$ . Define the angular momentum overlap integral,

$$4\pi\hat{R}_{if} = \frac{4\pi}{(2\pi\hbar)^3}. \quad (3.65)$$

(b)  $nl \rightarrow n'$

$$\begin{aligned} \sigma_{if}^{(ij)}(p_i) &= \frac{2\pi}{v_i^2 M_{ij}^2 (2\pi\hbar)^3} \int q_j dq_j \int d\mathbf{p} dE dL dE' dL' \delta\left(\frac{p^2}{2m} + V(r) - E\right) \\ &\quad \delta\left(\frac{(\mathbf{p} + \mathbf{q})^2}{2m} + V(r) - E'\right) |f_{ij}|^2 \int r^2 d\mathbf{r} \int d\cos\theta_r \delta(rp \sin\theta_r - L) \int d\phi_r, \end{aligned} \quad (3.66)$$

Define the angular momentum overlap integral,

$$4\pi\hat{R}'_{if} = \frac{1}{(2\pi\hbar)^3} \int d\cos\theta_r \delta(rp \sin\theta_r - L) \int d\phi_r. \quad (3.67)$$

(c)  $nl \rightarrow n'l'$

$$\begin{aligned} \sigma_{if}^{(ij)}(p_i) &= \frac{2\pi}{v_i^2 M_{ij}^2 (2\pi\hbar)^3} \int q_j dq_j \int d\mathbf{p} dE dL dE' dL' \delta\left(\frac{p^2}{2m} + V(r) - E\right) \\ &\quad \delta\left(\frac{(\mathbf{p} + \mathbf{q})^2}{2m} + V(r) - E'\right) |f_{ij}|^2 \int r^2 d\mathbf{r} \int d\cos\theta_r \delta(rp \sin\theta_r - L) \\ &\quad \int d\tilde{\phi}_r \delta(rp' \sin\tilde{\theta}_r - L'), \end{aligned} \quad (3.68)$$

where  $\tilde{\theta}_r$  and  $\tilde{\phi}_r$  are the zenith and azimuth angles of  $\mathbf{r}$  to  $\mathbf{p}'$ . Define the angular momentum overlap integral,

$$4\pi\hat{R}''_{if} = \frac{1}{(2\pi\hbar)^3} \int d\cos\theta_r \delta(rp \sin\theta_r - L) \int d\tilde{\phi}_r \delta(rp' \sin\tilde{\theta}_r - L'). \quad (3.69)$$

All three cases can be written in the same form with different angular momentum overlap integrals,  $\hat{R}_{if}^{(', '')}$ ,

$$\begin{aligned} \sigma_{if}^{(ij)}(p_i) &= \frac{2\pi}{v_i^2 M_{ij}^2} \int q_j dq_j \int r^2 d\mathbf{r} 4\pi\hat{R}_{if}^{(', '')} dE dL dE' dL' \int d\mathbf{p} \delta\left(\frac{p^2}{2m} + V(r) - E\right) \\ &\quad |f_{ij}|^2 \delta\left(\frac{(\mathbf{p} + \mathbf{q})^2}{2m} + V(r) - E'\right). \end{aligned} \quad (3.70)$$

$$(3.71)$$

Integrate and we get the form of total cross section for inelastic three-body collision ([10]),

$$\sigma_{if}^{(ij)}(p_i) = \frac{2\pi}{v_i^2 M_{ij}^2} \int q_j dq_j \int P(r, q) dr \left( \frac{1}{\pi} \int \frac{dg^2 |f_{ij}|^2}{[(g_+^2 - g^2)(g^2 - g_-^2)]^2} \right), \quad (3.72)$$

where

$$P(r, q) = \frac{2\pi m^2}{q} 4\pi \hat{R}_{if}^{('')} dE dL dE' dL'. \quad (3.73)$$

The limits for  $g^2$  are  $g_-^2$  and  $g_+^2$ . If the collision is elastic and  $|f_{ij}|$  is a constant, the integral

$$\int \frac{dg^2}{[(g_+^2 - g^2)(g^2 - g_-^2)]^2}, \quad (3.74)$$

results in  $\pi$ . Otherwise, the limits of  $g^2$  should be determined specifically.

## CHAPTER IV

### THE INELASTIC CROSS SECTION

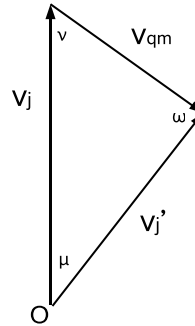
In the inelastic collision, the limits of the integration will be different. The energy change in the system is different from elastic collision, and the  $g'$  and  $g$  have different magnitudes. In the electron-ion,  $(j, k)$ , center of mass frame, the velocity of the incoming particle can be varying in any direction and in any magnitude. For the transition from  $n$  to  $n'$  and the incoming particle excited/deexcited from internal energy level  $i$  to level  $j$ , the change of total energy in the three body system,  $(\mathcal{E} + \Delta)$ , is fixed. We now discuss the range of variation of  $q$  and  $g$  with a given magnitude of  $v_i$ .

#### 4.1 *Determine the Limits*

In  $(j, k)$  center of mass frame, assume that electron's initial and final velocities  $v_j$  and  $v'_j$  are given. Define

$$\mathbf{v}_{qm} = \frac{\mathbf{q}}{m} = \frac{\mathbf{q}_j}{m_j} = \mathbf{v}'_j - \mathbf{v}_j, \quad (4.1)$$

and let  $\mu$ ,  $\nu$  and  $\omega$  be the angle in the triangles formed by  $v_j$ ,  $v'_j$  and  $v_{qm}$  as show in the



**Figure 4.1:** Definition of  $v_{qm}$ .

picture 4.1.  $O$  is the center of mass of  $(j, k)$  system. We have the relations

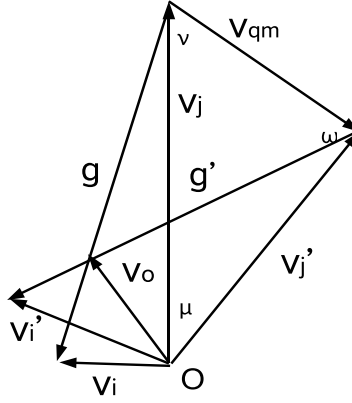
$$\cos \mu = \hat{\mathbf{v}}_i \cdot \hat{\mathbf{v}}'_i, \quad (4.2)$$

$$\cos \nu = -\hat{\mathbf{v}}_i \cdot \hat{\mathbf{v}}_{qm}, \quad (4.3)$$

and

$$\cos \omega = \hat{\mathbf{v}}'_i \cdot \hat{\mathbf{v}}_{qm}. \quad (4.4)$$

The limits of  $v_{qm}$  are  $|v_j - v'_j|$  and  $v_j + v'_j$ . We assume that  $v_{qm}$  is fixed as well.



**Figure 4.2:** Definition of  $v_o$ .

For elastic collision between  $i$  and  $j$ , the relative velocity of  $i$  and  $j$  does not change magnitude,

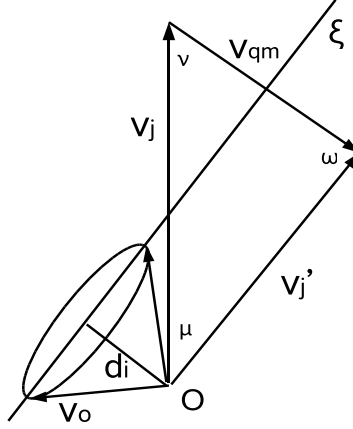
$$g = g'. \quad (4.5)$$

The velocity of the center-of-mass of  $(i, j)$ ,  $v_o$ , is pointing to the intersect of  $g$  and  $g'$  (figure 4.2). It is obvious that

$$|\mathbf{v}_o - \mathbf{v}_j| = |\mathbf{v}_o - \mathbf{v}'_j|. \quad (4.6)$$

#### 4.1.1 Solve from Fixed $v_o$

If the magnitude of  $v_o$  is known, the tip of  $v_o$  would be varying in a sphere. For the restriction (4.6), the tip of  $v_o$  can vary in a circle that is the intersection of the sphere and the plane  $\zeta$ , the perpendicular bisector of  $v_{qm}$  (figure 4.3). The distance between the  $(j, k)$



**Figure 4.3:** The tip of  $v_o$  can only vary in a circle.

center-of-mass  $O$  and the perpendicular bisector is defined as

$$d_i = \frac{1}{2} |v_j \cos \nu - v_j' \cos \omega|. \quad (4.7)$$

The angles can be expressed in terms of  $v_j$ ,  $v_j'$ , and  $v_{qm}$ , where

$$\cos \nu = \frac{v_j^2 + v_{qm}^2 - v_j'^2}{2v_j v_{qm}}, \quad (4.8)$$

$$\cos \omega = \frac{v_j'^2 + v_{qm}^2 - v_j^2}{2v_j' v_{qm}}. \quad (4.9)$$

So  $d_i$  can be written as

$$d_i = \frac{|v_j^2 - v_j'^2|}{2v_{qm}}. \quad (4.10)$$

Since  $v_{qm}$  has the maximum value of  $v_j + v_j'$ , in order to has a intersect with the plane  $\zeta$ ,  $v_o$  has a minimum value

$$v_o \geq d_i = \frac{|v_j - v_j'|}{2}. \quad (4.11)$$

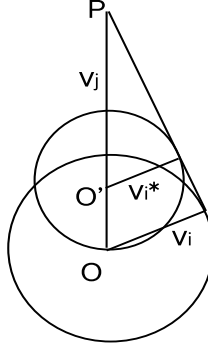
On the other hand, we can also write a restriction for  $v_{qm}$  for given  $v_j^{(l)}$  and  $v_o$ ,

$$v_{qm} \geq \frac{v_j^2 - v_j'^2}{2v_o}. \quad (4.12)$$

#### 4.1.2 Solve from Fixed $v_i$

The difficulty in the above discussion is that  $v_o$  is not such a quantity that can be determined directly. Instead, the kinetic energy or velocity of the incoming particle to the center-of-mass of  $(j, k)$  system is connected to the thermal energy or temperature. Thus, we should choose  $v_i$  as the given variable. With the magnitude fixed, the tip of  $v_i$  will be varying in a sphere with center  $O$ . Simultaneously,  $v_o$  is varying in a smaller sphere with radius  $v_i^*$  centered at point  $O'$  (figure 4.4), where

$$O'P = \frac{m_i}{m_i + m_j} OP. \quad (4.13)$$



**Figure 4.4:** The tips of  $v_i$  and  $v_i^*$  are varying in spheres.

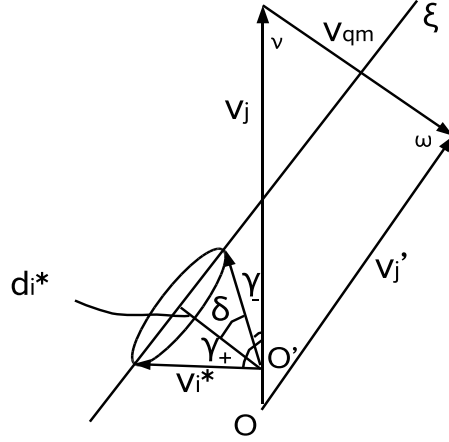
The radius of the smaller sphere  $\mathbf{v}_{i^*}$  is always parallel to  $\mathbf{v}_i$  and

$$v_i^* = \frac{m_i}{m_i + m_j} v_i. \quad (4.14)$$

The tip of  $v_o$  should be varying in a circle which is now the intersection of the smaller sphere  $O'$  and the perpendicular bisector of  $v_{qm}$ , plane  $\zeta$ . Define the distance between  $O'$  and plane  $\zeta$  as  $d_i^*$ , which can be found as

$$\begin{aligned} d_i^* &= \left| \frac{v_j^2 - v_j'^2}{2v_{qm}} - OO' \cos \nu \right| \\ &= \left| \frac{v_j^2 - v_j'^2}{2v_{qm}} - \frac{m_j}{m_i + m_j} v_j \frac{v_j^2 + v_{qm}^2 - v_j'^2}{2v_j v_{qm}} \right| \\ &= \left| \frac{m_i}{m_i + m_j} \frac{v_j^2 - v_j'^2}{2v_{qm}} - \frac{m_j}{m_i + m_j} \frac{v_{qm}}{2} \right|. \end{aligned} \quad (4.15)$$





**Figure 4.5:** The circle of the tip of  $v_o$  and the angle  $\delta$ ,  $\gamma_-$ , and  $\gamma_+$ .

The vector  $\mathbf{v}_i^*$  varies around  $d_i^*$ , and the variation have a constant angle  $\delta$  between them as shown in figure (4.5). Thus, the angle between  $v_i^*$  and  $v_j$ , defined as  $\gamma$ , has the range  $[\gamma_-, \gamma_+]$ , where

$$\gamma_- = |\delta - \nu| \quad \gamma_+ = \delta + \nu. \quad (4.16)$$

#### 4.1.3 Inelastic Collision

For inelastic collision,  $g'$  has different magnitude with  $g$ . The kinetic energy lost in system  $(i, j)$  is  $\Delta$ , as in

$$\Delta = \frac{1}{2}m_{ij}(g^2 - g'^2). \quad (4.17)$$

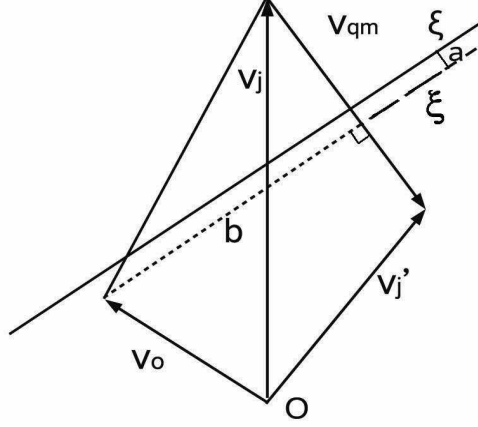
Therefore, the tip of  $\mathbf{v}_o$  is no longer in the perpendicular bisector of  $\mathbf{v}_{qm}$ . From the figure (4.2), one can obtain the relation

$$|\mathbf{v}_o - \mathbf{v}_j| = \frac{m_i}{m_i + m_j}g, \quad (4.18)$$

$$|\mathbf{v}_o - \mathbf{v}_j'| = \frac{m_i}{m_i + m_j}g'. \quad (4.19)$$

So we can relate them to the energy lost  $\Delta$

$$\begin{aligned} |\mathbf{v}_o - \mathbf{v}_j|^2 - |\mathbf{v}_o - \mathbf{v}_j'|^2 &= \left(\frac{m_i}{m_i + m_j}\right)^2(g^2 - g'^2) \\ &= \frac{2m_i\Delta}{(m_i + m_j)m_j}. \end{aligned} \quad (4.20)$$



**Figure 4.6:** Distance  $a$  and  $b$ .

Suppose the distance from the tip of  $\mathbf{v}_o$  to the perpendicular bisector of  $\mathbf{v}_{qm}$  is  $a$  and the distance to  $\mathbf{v}_{qm}$  is  $b$  (figure 4.6). Then the expression above can be rewritten as

$$\begin{aligned} |\mathbf{v}_o - \mathbf{v}_j|^2 - |\mathbf{v}_o - \mathbf{v}_j'|^2 &= b^2 + \left(\frac{v_{qm}}{2} + a\right)^2 - b^2 + \left(\frac{v_{qm}}{2} - a\right)^2 \\ &= 2v_{qm}a. \end{aligned} \quad (4.21)$$

For a fixed energy lost  $\Delta$ ,  $a$  is a constant,

$$a = \frac{m_i \Delta}{m_j(m_i + m_j)v_{qm}} = \frac{m_{ij}\Delta}{m_j^2 v_{qm}}. \quad (4.22)$$

The tip of  $\mathbf{v}_o$  is varying in the plane  $\xi$  that has distance  $a$  to the perpendicular bisector  $\zeta$ .

Let  $d_i^+$  be the distance from  $O'$  to plane  $\xi$  (figure 4.7), we have

$$\begin{aligned} d_i^+ &= d_i^* - a \\ &= \frac{v_j^{*2} - v_j'^2}{2v_{qm}^*} - \frac{v_{qm} - v_{qm}^*}{2} - \frac{m_{ij}\Delta}{m_j^2 v_{qm}}. \end{aligned} \quad (4.23)$$

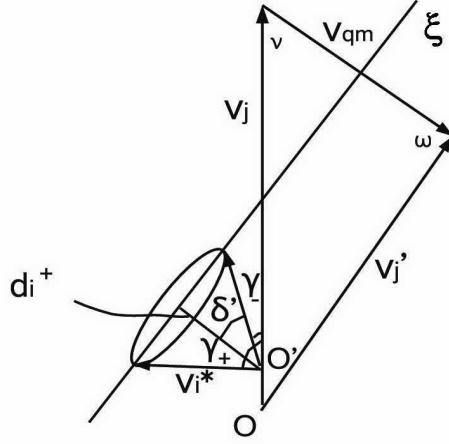
The angle between  $\mathbf{v}_i^*$  and  $d_i^+$ , which is not  $\delta$ , can be defined as  $\delta'$ , where

$$\cos \delta' = \frac{d_i^+}{v_i^*} = \frac{v_j^2 - v_j'^2}{2v_{qm}v_i} - \frac{m_j v_{qm}}{2m_i v_i} - \frac{\Delta}{m_j v_{qm} v_i}. \quad (4.24)$$

Then the range of  $\gamma$ ,  $[\gamma_-, \gamma_+]$  becomes

$$\gamma_- = |\delta' - \nu|, \quad (4.25)$$

$$\gamma_+ = \delta' + \nu. \quad (4.26)$$



**Figure 4.7:** Distance  $d_i^+$  to plane  $\xi$  and angle  $\delta'$ .

#### 4.1.4 The Limits of $g^2$

Since  $\mathbf{v}_i^*$  and  $\mathbf{v}_i$  are parallel, the angle between  $\mathbf{v}_i$  and  $\mathbf{v}_j$  is also  $\gamma$ .  $v_i$  and  $v_j$  are fixed and  $\mathbf{g} = \mathbf{v}_i - \mathbf{v}_j$ . Thus  $\mathbf{g}$  varies with  $\gamma$ . So the range of  $g^2$  is

$$[v_i^2 + v_j^2 - 2v_i v_j \cos \gamma_-, v_i^2 + v_j^2 - 2v_i v_j \cos \gamma_+], \quad (4.27)$$

where the limits will be switched when  $\cos \gamma_+ < \cos \gamma_-$ . The magnitudes of velocities,  $v_j$  and  $v_{qm}$ , are not used as the variables in the integrations of the cross section. They can be substituted by expressions in terms of  $p$  and  $q$  or  $r$  and  $q$ . The expressions of  $\cos \nu$ ,  $\cos \delta'$  and the limits of  $g^2$  need to be changed too.

$\nu$  is the angle between  $\mathbf{v}_j$  and  $\mathbf{v}_{qm}$  and is also the angle between  $\mathbf{p}$  and  $\mathbf{q}$ . We can write

$$\cos \nu = \frac{p^2 + q^2 - p'^2}{2pq} = \frac{v^2 + v_{qm}^2 - v'^2}{2vv_{qm}} = -\frac{2m\mathcal{E} - q^2}{2pq}. \quad (4.28)$$

Compare to its previous expression, we obtain the relation

$$\begin{aligned} \frac{v^2 + v_{qm}^2 - v'^2}{2vv_{qm}} &= \frac{v_j^2 + v_{qm}^2 - v_j'^2}{2v_j v_{qm}} \\ v_j^2 - v_j'^2 &= \frac{m_k}{m_j + m_k}(v^2 - v'^2) - \frac{m_j}{m_j + m_k}v_{qm}^2. \end{aligned} \quad (4.29)$$

We then can get the expression of  $v_j^2 - v_j'^2$  in terms of  $\mathcal{E}$  and  $q_j$

$$v_j^2 - v_j'^2 = -\frac{2\mathcal{E}}{m_j} - \frac{q_j^2}{m_j(m_j + m_k)}, \quad (4.30)$$

where

$$\mathcal{E} = E' - E = \frac{1}{2}m(v'^2 - v^2). \quad (4.31)$$

This relation can be applied to the expression of  $\cos \delta'$  too,

$$\begin{aligned} \cos \delta' &= \frac{v_j^2 - v_j'^2}{2v_{qm}v_i} - \frac{m_j v_{qm}}{2m_i v_i} - \frac{\Delta}{m_j v_{qm} v_i} \\ &= \frac{-2\mathcal{E} - \frac{q_j^2}{m_j + m_k}}{2v_i q_j} - \frac{q_j^2}{2m_i v_i q_j} - \frac{\Delta}{v_i q_j} \\ &= -\frac{\mathcal{E} + \Delta}{v_i q_j} - \frac{q_j}{2\mu_i v_i}. \end{aligned} \quad (4.32)$$

In the cases of  $n - n'$  and  $nl - n'l'$ , the integration is taken with respect to  $r$  instead of  $p$ .  $p$  is substituted with

$$p = \sqrt{2m(E - V)} = \sqrt{2m\left(\frac{-1}{2n^2} + \frac{e^2}{r}\right)} = \sqrt{\frac{2m}{r} - \frac{m}{n^2}}. \quad (4.33)$$

Atomic unit is applied to the expression, and for particle  $j$  is electron,  $m_j = 1$ . So  $v_j$  can be written as

$$v_j = \frac{p}{m_j} = \sqrt{\frac{2m}{r} - \frac{m}{n^2}}, \quad (4.34)$$

$\cos \nu$  can be written with  $q_j$  instead of  $q$ , and

$$\cos \nu = -\frac{2m\mathcal{E} - q^2}{2pq} = -\frac{1}{p}\left(\frac{\mathcal{E}}{q_j} - \frac{mq_j}{2}\right). \quad (4.35)$$

We then can obtain the limits of  $g^2$ . Define

$$\begin{aligned} g_{\pm} &= (v_i^2 + v_j^2 - 2v_i v_j \cos \gamma_{\pm})^{1/2} \\ &= \left(v_i^2 + \frac{2m}{r} - \frac{m}{n^2} - 2v_i \sqrt{\frac{2m}{r} - \frac{m}{n^2}} \cos \gamma_{\pm}\right)^{1/2}, \end{aligned} \quad (4.36)$$

where

$$\cos \gamma_{\pm} = \cos \left( \arccos \left( -\frac{1}{\sqrt{\frac{2m}{r} - \frac{m}{n^2}}} \left( \frac{\mathcal{E}}{q_j} - \frac{mq_j}{2} \right) \right) \pm \arccos \left( -\frac{\mathcal{E} + \Delta}{v_i q_j} - \frac{q_j}{2\mu_i v_i} \right) \right). \quad (4.37)$$

The absolute value sign for  $\gamma_- = |\delta' - \nu|$  was dropped since *cosine* is an even function. The range of  $g^2$  can be expressed as

$$[g_l = \min(g_-, g_+), \quad g_u = \max(g_-, g_+)]. \quad (4.38)$$

For inelastic collision, the definition of  $\Delta$  gives another restriction of  $g^2$ . To let  $g' > 0$ , for a given  $\Delta$ , the  $1/2M_{ij}g^2$  must be larger than  $\Delta$

$$g^2 > \frac{2\Delta}{m_{ij}}. \quad (4.39)$$

For the case

$$g_{up}^2 < \frac{2\Delta}{m_{ij}}, \quad (4.40)$$

the integration of the cross section has no value. In other cases, the range of  $g^2$  is

$$[g_l = \min(\frac{2\Delta}{m_{ij}}, \min(g_-, g_+)), \quad g_u = \max(g_-, g_+)]. \quad (4.41)$$

#### 4.1.5 The Limits of $q_j$

We can obtain the limits of  $q_j$  from the expression of  $\cos \delta'$ ,

$$\cos \delta' = \frac{d_i^+}{v_i^*} = \left| \frac{\mathcal{E} + \Delta}{v_i q_j} + \frac{q_j}{2\mu_i v_i} \right| \leq 1, \quad (4.42)$$

where  $\mathcal{E}$ ,  $\Delta$ ,  $v_i$ , and  $\mu_i$  are given.  $v_i$ ,  $\mu_i$ , and  $q_j$  are larger than 0 and the inequality above can be multiplied by  $\mu_i v_i q_j$  and the inequality changes into:

$$\begin{cases} \frac{q_j^2}{2} - \mu_i v_i q_j + \mu_i(\mathcal{E} + \Delta) \leq 0, \\ \frac{q_j^2}{2} + \mu_i v_i q_j + \mu_i(\mathcal{E} + \Delta) \geq 0, \end{cases} \quad (4.43)$$

with the range of  $q_j$

$$\begin{cases} [\mu_i v_i - \sqrt{\mu_i^2 v_i^2 - 2\mu_i(\mathcal{E} + \Delta)}, \mu_i v_i + \sqrt{\mu_i^2 v_i^2 - 2\mu_i(\mathcal{E} + \Delta)}] \cap \\ (-\infty, -\sqrt{\mu_i^2 v_i^2 - 2\mu_i(\mathcal{E} + \Delta)} - \mu_i v_i] \cup [\sqrt{\mu_i^2 v_i^2 - 2\mu_i(\mathcal{E} + \Delta)} - \mu_i v_i, \infty). \end{cases} \quad (4.44)$$

The negative set should be discarded. So for  $\mathcal{E} + \Delta > 0$ , the range of  $q_j$  is

$$[\mu_i v_i - \sqrt{\mu_i^2 v_i^2 - 2\mu_i(\mathcal{E} + \Delta)}, \mu_i v_i + \sqrt{\mu_i^2 v_i^2 - 2\mu_i(\mathcal{E} + \Delta)}]. \quad (4.45)$$

For  $\mathcal{E} + \Delta < 0$ , the range changes into

$$[\sqrt{\mu_i^2 v_i^2 - 2\mu_i(\mathcal{E} + \Delta)} - \mu_i v_i, \mu_i v_i + \sqrt{\mu_i^2 v_i^2 - 2\mu_i(\mathcal{E} + \Delta)}]. \quad (4.46)$$

Combine these two inequalities, we have the expression of the range of  $q_j$ ,

$$\left[ \left| \mu_i v_i - \sqrt{\mu_i^2 v_i^2 - 2\mu_i(\mathcal{E} + \Delta)} \right|, \mu_i v_i + \sqrt{\mu_i^2 v_i^2 - 2\mu_i(\mathcal{E} + \Delta)} \right]. \quad (4.47)$$

#### 4.1.6 The Limits of $v_i$

In the above discussion, the square root must have a real value. We can get a restriction of  $v_i$

$$\mu_i^2 v_i^2 - 2\mu_i(\mathcal{E} + \Delta) \geq 0. \quad (4.48)$$

So for  $\mathcal{E} + \Delta > 0$ , the range of  $v_i$  is

$$[\sqrt{2(\mathcal{E} + \Delta)/\mu_i}, \infty). \quad (4.49)$$

For  $\mathcal{E} + \Delta < 0$ , the range of  $v_i$  is

$$[0, \infty). \quad (4.50)$$

#### 4.1.7 The Limits of $p$ , $q_j$ of Transition $nl \rightarrow n'$

When we calculate the cross section for transition  $nl \rightarrow n'$ , the integral is taken over  $p$  instead of  $r$ . The limits of integration over  $p$  were given by Vrinceanu and Flannery (1999) [13],

$$P_{nl,n'}(q) \frac{2(2l+1)}{\pi q n'^3} \int_{p_{min}}^{p_+} \frac{n}{p(1+n^2 p^2)^2} \left[ 1 - \left( \frac{L(1+n^2 p^2)}{2n^2 p} \right)^2 \right]^{-1/2}, \quad (4.51)$$

where

$$p_{min} = \left[ p_0 - \left| q^2 + \frac{1}{n'^2} - \frac{1}{n^2} \right| / 2q, p_- \right], \quad (4.52)$$

$$p_{\pm} = \left( 1 \pm \left( 1 - \frac{L^2}{n^2} \right)^{1/2} \right) / L, \quad (4.53)$$

$$L = l + 1/2, \quad (4.54)$$

$$\text{and } q = \frac{m}{m_j} q_j. \quad (4.55)$$

Following their discussion we find another restriction for  $q$ ,

$$q \in \left[ \left| p_+ - \sqrt{p_+^2 - 2\mathcal{E}} \right|, p_+ + \sqrt{p_+^2 - 2\mathcal{E}} \right]. \quad (4.56)$$

So the limits of  $q_j$  of transition  $nl \rightarrow n'$  can be written as

$$q_{min} = \max \left[ q_{j-}, \left| p_+ - \sqrt{p_+^2 + 2\mathcal{E}} \right| \right], \quad (4.57)$$

$$q_{max} = \min \left[ q_{j+}, p_+ + \sqrt{p_+^2 + 2\mathcal{E}} \right], \quad (4.58)$$

where

$$q_{j\pm} = |\mu_i v_i \pm \sqrt{\mu_i^2 v_i^2 - 2\mu_i(\mathcal{E} + \Delta)}|. \quad (4.59)$$

## 4.2 Comparison to Flannery's Elastic Formulation

We have followed the theory of Flannery (2000) [10] to determine the cross section of inelastic collision of three body recombination. It has almost the same expressions although with different limitations. We should get the same result if the inelastic energy lost  $\Delta$  is set to be zero. However, there are some differences in the basic setting. We now point out those differences and discuss their effects.

### 4.2.1 Comparison of the Limits of $g^2$

The above discussion of the  $g^2$  limits should have the same expression when the energy lost due to the inelastic collision  $\Delta$  is set to zero. The limits of  $g^2$  in [10] is written as

$$g_{\pm}^2 = v_i^2 + v_j^2 - 2v_i v_j \cos(\tilde{\theta}^* \pm \theta_i), \quad (4.60)$$

where

$$\cos \theta_i = \frac{2\mu_i \mathcal{E} + q_j^2}{2p_i^* q_j}, \quad (4.61)$$

$$\cos \tilde{\theta}^* = \frac{2m\mathcal{E} - q^2}{2pq}, \quad (4.62)$$

and

$$p_i^* = \mu_i v_i. \quad (4.63)$$

The cosines of the angles  $\theta_i$  and  $\tilde{\theta}^*$  are just the additive inverse of the angles in our discussion,  $\nu$  and  $\delta'$ , when  $\Delta$  is set to zero,

$$\cos \delta' = -\frac{\mathcal{E}}{v_i q_j} - \frac{q_j}{2\mu_i v_i} = -\cos \theta_i, \quad (4.64)$$

$$\cos \nu = -\frac{2m\mathcal{E} - q^2}{2pq} = -\cos \tilde{\theta}^*. \quad (4.65)$$

Therefore  $\delta'$  and  $\nu$  are just the supplements of  $\theta_i$  and  $\tilde{\theta}^*$

$$\delta' = \pi - \theta_i, \quad (4.66)$$

$$\nu = \pi - \tilde{\theta}^*. \quad (4.67)$$

The cosine functions in the limits of  $g^2$  can be expressed as

$$\begin{aligned} \cos(\delta' \pm \nu) &= \cos(\pi - \theta_i \pm (\pi - \tilde{\theta}^*)) \\ &= \cos(\theta_i \pm \tilde{\theta}^*), \end{aligned} \quad (4.68)$$

which is equivalent to Flannery's expression.

#### 4.2.2 The Definition of $p_i^{(')}$

Our definitions of  $g^{(')}$ ,  $q$ , and  $q_j$  (magnitude) are the same as the definitions defined by Flannery (2000) [10]. We have also got the same expression of  $q_j$  in terms of  $\mathbf{p}_i$  and  $\mathbf{p}'_i$

$$\mathbf{q}_j = \mathbf{p}_i - \mathbf{p}'_i = \mathbf{p}'_j - \mathbf{p}_j. \quad (4.69)$$

However the definitions of  $\mathbf{p}_i$  and  $\mathbf{p}'_i$  are actually different. We adopted the particle mass  $m_i$  to define

$$\mathbf{p}_i^{(')} = m_i \mathbf{v}_i^{(')}, \quad (4.70)$$

where  $v_i^{(i)}$  are the velocities of the incoming particle  $i$  to the initial center of mass of  $(j, k)$  system. Flannery (2000) used the relative mass  $\mu_i$  instead [10],

$$\mathbf{p}_{i,F}^{(')} = \mu_i \mathbf{v}_i^{(')}, \quad (4.71)$$



where  $\mathbf{p}_{i,\mathbf{F}}^{(')}$  are actually the relative momenta of  $i$  and the center of mass of  $(j, k)$  in the  $(i, j, k)$  center of mass frame.  $\mathbf{v}_i^{(')}$  are the relative velocities of the particle  $i$  to the center of mass of  $(j, k)$ ,

$$v_i'' = \mathbf{v}_i' - \mathbf{V}', \quad (4.72)$$

where  $\mathbf{V}'$  is the final-to-initial relative velocity of the center of mass of  $(j, k)$  system,

$$\mathbf{V}' = \frac{m_j}{m_j + m_k} \mathbf{v}_{\mathbf{qm}} = \frac{q_j}{m_j + m_k}. \quad (4.73)$$

$\mathbf{p}_{i,\mathbf{F}}^{(')}$  also hold the equation as (4.69)

$$\begin{aligned} \mathbf{p}_{i,\mathbf{F}} - \mathbf{p}_{i,\mathbf{F}}' &= \mu_i \mathbf{v}_i - \mu_i (\mathbf{v}_i' - \mathbf{V}') \\ &= \mu_i \mathbf{v}_i - \mu_i \left( \mathbf{v}_i' - \frac{m_j}{m_j + m_k} \mathbf{v}_{\mathbf{qm}} \right) \\ &= \mu_i \mathbf{v}_i - \mu_i \mathbf{v}_i' + \frac{m_i \mu_i}{m_j + m_k} (\mathbf{v}_i - \mathbf{v}_i') \\ &= \mu_i \left( 1 + \frac{\mu_i}{m_j + m_k} \right) (\mathbf{v}_i - \mathbf{v}_i') \\ &= m_i \mathbf{v}_i - m_i \mathbf{v}_i' \\ &= \mathbf{p}_i - \mathbf{p}_i' \\ &= \mathbf{q}_i. \end{aligned} \quad (4.74)$$

The energy conservation equation can be expressed as

$$\begin{aligned} \frac{1}{2} m_i v_i^2 + \frac{1}{2} m v^2 &= \frac{1}{2} \mu_i v_i^2 + \frac{1}{2} (m_j + m_k) v_c^2 + \frac{1}{2} m v^2 \\ &= \frac{1}{2} \mu_i v_i'^2 + \frac{1}{2} (m_j + m_k) v_c^2 + \frac{1}{2} m v'^2 + \Delta, \end{aligned} \quad (4.75)$$

where  $m$  and  $v^{(')}$  are the relative mass and velocities of  $j, k$  system,  $v_c$  is the velocity of the center of mass of all three bodies, and  $\Delta$  is the internal energy change of particle  $i$ . Thus  $v_i'^2$  can be expressed as

$$v_i'^2 = v_i^2 - 2 \frac{\mathcal{E} + \Delta}{\mu_i}. \quad (4.76)$$

When  $v_i$ ,  $\mathcal{E}$ , and  $\Delta$  are given,  $v_i''$  is fixed, and  $p_i'$  is fixed as well,

$$p_i' = \mu_i v_i'' = \sqrt{\mu_i^2 v_i^2 - 2 \mu_i (\mathcal{E} + \Delta)}. \quad (4.77)$$

The range of  $q_j$  that given by Flannery (2000) [10] is

$$[|p_i - p_i'|, \quad p_i + p_i'] , \quad (4.78)$$

which is the same result as equation (4.59) as we expected.

The energy conservation equation that we set up is,

$$\frac{1}{2}m_i v_i^2 + \frac{1}{2}m v^2 = \frac{1}{2}m_i v_i'^2 + \frac{1}{2}(m_j + m_k)V^2 + \frac{1}{2}m v'^2 + \Delta. \quad (4.79)$$

For a given  $\mathbf{v}_i$ ,  $\mathcal{E}$ , and  $\Delta$ ,  $v_i'^2$  depends on  $q_j$ ,

$$v_i'^2 = v_i^2 - 2\frac{\mathcal{E} + \Delta}{m_i} - \frac{q_j^2}{m_i(m_j + m_k)}. \quad (4.80)$$

As  $q_i$  is changing in the range of

$$[q_-, q_+] = \left[ |\mu_i v_i - \sqrt{\mu_i^2 v_i^2 - 2\mu(\mathcal{E} + \Delta)}|, \mu_i v_i + \sqrt{\mu_i^2 v_i^2 - 2\mu(\mathcal{E} + \Delta)} \right], \quad (4.81)$$

$v_j'$  is not a constant, and  $p_i'$  is varying in the range

$$p_i' \in \left[ \sqrt{\mu_i^2 v_i^2 - 2\mu(\mathcal{E} + \Delta)} + \mu_i v_i - m_i v_i, \sqrt{\mu_i^2 v_i^2 - 2\mu(\mathcal{E} + \Delta)} - \mu_i v_i + m_i v_i \right], \quad (4.82)$$

which is slightly different from the definition by Flannery (2000) [10]. In a ion-electron recombination, particle  $j$ , the electron has significantly smaller mass than  $i$  or  $k$ . The difference between  $\mu_i$  and  $m_i$  can be ignored. This difference of setting up will not change the result of the total cross section calculation for  $p_i'$  is not in the expression. The integration interval with respect to  $p_i$  is from zero to infinity. The two different definitions of  $p_i$  and  $p_{i,F}'$  will have the same result.

### 4.3 The General Expression of the Inelastic Cross Sections

Now the parameters of the calculation of the cross section have been found. We can then write down the expressions of the cross section. The general expression of total cross section is

$$\begin{aligned} \sigma_{if}^{(ij)}(p_i) &= \frac{2\pi}{v_i^2 M_{ij}^2} \int q_j dq_j \int r^2 d\mathbf{r} 4\pi \hat{R}_{if} dE dL dE' dL' \Theta(r, q) \\ &\quad \frac{2\pi m^2}{q} \left( \frac{1}{\pi} \int \frac{dg^2 |f_{ij}|^2}{[(g_+^2 - g^2)(g^2 - g_-^2)]^{1/2}} \right) \\ &= \frac{2\pi}{v_i^2 M_{ij}^2} \int q_j dq_j \int P(r, q) dr \left( \frac{1}{\pi} \int \frac{dg^2 |f_{ij}|^2}{[(g_+^2 - g^2)(g^2 - g_-^2)]^{1/2}} \right), \end{aligned} \quad (4.83)$$

where

$$P(r, q) = \frac{2\pi m^2}{q} 4\pi \hat{R}_{if} dE dL dE' dL', \quad (4.84)$$

is the form factor. The limits of  $g^2$  are

$$[g_m^2, g_+^2], \quad (4.85)$$

where

$$g_m^2 = \max(g_-^2, 2\Delta/M_{ij}), \quad (4.86)$$

$$g_{\pm} = v_i^2 + v_j^2 - 2v_i v_j \cos \gamma_{\pm}, \quad (4.87)$$

$$v_j^2 = m\left(\frac{2}{r} - \frac{1}{n^2}\right), \quad (4.88)$$

$$\gamma_- = |\delta - \nu| \quad \gamma_+ = \delta + \nu, \quad (4.89)$$

$$\cos \delta = \frac{2\mu_i(\mathcal{E} + \Delta) + q_j^2}{2\mu_i v_i q_j}, \quad (4.90)$$

$$\cos \nu = \frac{2\mathcal{E} - m q_j^2}{2p q_j} = \frac{\mathcal{E} - m q_j^2/2}{q_j \sqrt{m(2/r - 1/n^2)}}. \quad (4.91)$$

If the scattering amplitude  $|f_{ij}|$  is a constant, the integration over  $g^2$  gets  $\pi$  and we get  $|f_{ij}|$  in the parentheses. Let  $\sigma_0$  be the differential cross section of the two-body collision between the electron and the incoming molecular. We have

$$\sigma_0 = \omega |f_{ij}|^2, \quad (4.92)$$

where

$$\omega = \frac{g'}{g}. \quad (4.93)$$

We can express the general form of the total cross section in terms of  $\sigma_0$ ,

$$\sigma_{if}^{(ij)}(p_i) = \frac{2\pi}{v_i^2 M_{ij}^2} \int q_j dq_j \int P(r, q) dr \left( \frac{1}{\pi} \int \frac{dg^2 (\sigma_0(g)/\omega)}{[(g_+^2 - g^2)(g^2 - g_-^2)]^{1/2}} \right). \quad (4.94)$$

#### 4.3.1 $n \rightarrow n'$

For translation from  $n \rightarrow n'$ , the form factor is

$$\begin{aligned}
P_{nn'}(r, q)dr &= \frac{2\pi m^2}{q} 4\pi \hat{R} r^2 dr dE dE' \\
&= \frac{2\pi m}{q_j} 4\pi r^2 dr \frac{\hbar \hbar}{(2\pi \hbar)^3 n^3 n'^3} \\
&= \frac{mr^2 dr}{q_j \pi n^3 n'^3},
\end{aligned} \tag{4.95}$$

where  $dE^{(\prime)}$  take the value  $1/n^{(\prime)3}$  in atomic units. The cross section is

$$\sigma_{if}^{(ij)}(p_i) = \frac{2m}{M_{ij}^2 v_i^2 \pi n^3 n'^3} \int_{q_{j-}}^{q_{j+}} dq_j \int_0^{r^*} r^2 dr \int_{g_m^2}^{g_+^2} \frac{(\sigma_0(g)/\omega) dg^2}{[(g_+^2 - g^2)(g^2 - g_-^2)]^{1/2}}, \tag{4.96}$$

where

$$r^* = \frac{8mq^2}{q^4 - 4mq^2(E' + E) + 4m^2(E' - E)^2} \tag{4.97}$$

$$= \frac{8mq_j^2}{m^2 q_j^4 + 2mq_j^2(\frac{1}{n^2} + \frac{1}{n'^2}) + (2\mathcal{E})^2},$$

$$g_m^2 = \max(g_-^2, 2\Delta/M_{ij}), \tag{4.98}$$

$$g_{\pm} = (v_i^2 + \frac{2m}{r} - \frac{m}{n^2} - 2v_i \sqrt{\frac{2m}{r} - \frac{m}{n^2}} \cos \gamma_{\pm}). \tag{4.99}$$

#### 4.3.2 $nl \rightarrow n'$

For the transition from  $nl \rightarrow n'$ , the form factor is ([13])

$$P_{nl n'}(p, q) = \frac{2L}{\pi q n'^3} \frac{n}{p(1 + n^2 p^2)^2} (1 - (\frac{L(1 + n^2 p^2)}{2n^2 p})^2)^{-\frac{1}{2}}. \tag{4.100}$$

The cross section can be written as

$$\begin{aligned}
\sigma_{if}^{(ij)}(v_i) &= \frac{8n^3 L}{M_{ij}^2 v_i^2 \pi n'^3} \int_{q_{min}}^{q_{max}} dq_j \int_{p_{min}}^{p^+} \frac{dp (1 + n^2 p^2)^{-2}}{\sqrt{4n^4 p^2 - L^2 (1 + n^2 p^2)^2}} \\
&\quad \int_{g_m^2}^{g_+^2} \frac{(\sigma_0(g)/\omega) dg^2}{[(g_+^2 - g^2)(g^2 - g_-^2)]^{1/2}},
\end{aligned} \tag{4.101}$$

where

$$g_m^2 = \max(g_-^2, 2\Delta/M_{ij}), \quad (4.102)$$

$$p_{min} = \max \left[ p_0 = |q^2 + \frac{1}{n'^2} - \frac{1}{n^2}|/2q, p_- \right], \quad (4.103)$$

$$p_{\pm} = (1 \pm (1 - L^2/n^2)^{1/2})/L, \quad (4.104)$$

$$q_{min} = \max \left[ q_{j-}, p_+ - \sqrt{p_+^2 + 2\mathcal{E}} \right], \quad (4.105)$$

$$q_{max} = \min \left[ q_{j+}, p_+ + \sqrt{p_+^2 + 2\mathcal{E}} \right]. \quad (4.106)$$

There are some restrictions about transition  $nl \rightarrow n'$ . First,  $n'$  has a lower limit, ([13])

$$n' > n_- = \frac{L}{\sqrt{2(1 + \sqrt{1 - L^2/n^2})}}. \quad (4.107)$$

Second, the intersection of  $[q_{j-}, q_{j+}]$  and  $[p_+ - \sqrt{p_+^2 + 2\mathcal{E}}, p_+ + \sqrt{p_+^2 + 2\mathcal{E}}]$  must not be empty, which requires

$$q_{j-} < p_+ + \sqrt{p_+^2 + 2\mathcal{E}}, \quad (4.108)$$

and

$$q_{j+} > p_+ - \sqrt{p_+^2 + 2\mathcal{E}}. \quad (4.109)$$

### 4.3.3 $nl \rightarrow n'l'$

For the transition from  $nl \rightarrow n'l'$ , the form factor is, ([13])

$$P_{nl n' l'}(p, q) = \frac{2LL'}{\pi^2 n^3 n'^3} \int_{R_{min}}^{R_{max}} \frac{1}{q} \frac{dr}{r^2 \dot{r} \dot{r}'} (G_{if}^+(r, q) + G_{if}^-(r, q)), \quad (4.110)$$

where

$$L = l + 1/2, \quad L' = l' + 1/2, \quad (4.111)$$

$$R_{min} = \max[R_i^-, R_f^-], \quad R_{max} = \min[R_i^+, R_f^+], \quad (4.112)$$

$$\dot{r}^{(\prime)} = \sqrt{\frac{2}{r} - \left(\frac{1}{n^{(\prime)2}} + \frac{L^{(\prime)2}}{r^2}\right)}, \quad (4.113)$$

$$r^2 \dot{r} \dot{r}' = \sqrt{(R_i^+ - r)(r - R_i^-)} \sqrt{(R_f^+ - r)(r - R_f^-)} / (nn'), \quad (4.114)$$

$$R_i^\pm = n^2 \left(1 \pm \sqrt{1 - \frac{L^2}{n^2}}\right), \quad (4.115)$$

$$R_f^\pm = n'^2 \left(1 \pm \sqrt{1 - \frac{L'^2}{n'^2}}\right), \quad (4.116)$$

$$G_{if}^\pm = \frac{1}{\sqrt{(q^2 - A_\pm^2)(B_\pm^2 - q^2)}}, \quad (4.117)$$

$$A_\pm^2 = \frac{(L - L')^2}{r^2} + m^2(\dot{r} \pm \dot{r}')^2, \quad (4.118)$$

$$B_\pm^2 = \frac{(L + L')^2}{r^2} + m^2(\dot{r} \pm \dot{r}')^2. \quad (4.119)$$

The cross section can be written as

$$\begin{aligned} \sigma_{if}^{(ij)}(v_i) &= \frac{4LL'}{M_{ij}^2 m^3 v_i^2 \pi n^3 n'^3} \int_{R_{min}}^{R_{max}} \frac{dr}{r^2 \dot{r} \dot{r}'} \\ &\quad \int dq dq (G_{if}^+(r, q) + G_{if}^-(r, q)) \int_{g_m^2}^{g_+^2} \frac{(\sigma_0(g)/\omega) dg^2}{[(g_+^2 - g^2)(g^2 - g_-^2)]^{1/2}} \\ &= \frac{4LL'}{M_{ij}^2 m^3 v_i^2 \pi n^2 n'^2} \int_{R_{min}}^{R_{max}} \frac{dr}{\sqrt{(R_i^+ - r)(r - R_i^-)} \sqrt{(R_f^+ - r)(r - R_f^-)}} \\ &\quad \left( \int_{\max(q_-, A_+)}^{\min(q_+, B_+)} \frac{dq}{[(q^2 - A_+^2)(B_+^2 - q^2)]^{1/2}} \int_{g_m^2}^{g_+^2} \frac{(\sigma_0(g)/\omega) dg^2}{[(g_+^2 - g^2)(g^2 - g_-^2)]^{1/2}} \right. \\ &\quad \left. + \int_{\max(q_-, A_-)}^{\min(q_+, B_-)} \frac{dq}{[(q^2 - A_-^2)(B_-^2 - q^2)]^{1/2}} \int_{g_m^2}^{g_+^2} \frac{(\sigma_0(g)/\omega) dg^2}{[(g_+^2 - g^2)(g^2 - g_-^2)]^{1/2}} \right), \end{aligned} \quad (4.120)$$

where

$$g_m^2 = \max(g_-^2, 2\Delta/M_{ij}), \quad (4.121)$$

and

$$g_\pm^2 = (v_i^2 + \frac{2m}{r} - \frac{m}{n^2} - 2v_i \sqrt{\frac{2m}{r} - \frac{m}{n^2}} \cos \gamma_\pm). \quad (4.122)$$

## CHAPTER V

### RATE COEFFICIENT $K$ AND DETAILED BALANCING PRINCIPLE

#### 5.1 *Rate Coefficient* $K(n, n')$

For the process



the expression of rate coefficient  $K(n, n')$  has both elastic and inelastic terms

$$K(n, n') = K_0(n, n') + \frac{1}{f_z(T)} \sum_i \sum_{j \neq i} \omega_i \exp(-\epsilon_i) K(n, n'|i, j), \quad (5.2)$$

where  $K_0(n, n')$  is the rate coefficient of the elastic collision, and  $K(n, n'|i, j)$  is of the inelastic collision in which the molecule's internal energy changes from level  $i$  to level  $j$ .  $f_z(T)$  is the internal partition function. We write the general expression of the rate coefficient as  $K(\mathcal{E}, \Delta)$ , where  $\mathcal{E}$  is the energy change in the atom and  $\Delta$  is the energy change in the molecule (Defined in (3.47), (3.44)). In elastic collision,  $\Delta$  is zero.

The rate coefficient  $K(\mathcal{E}, \Delta)$  can be obtain by integrating cross sections over the velocities of the incoming particle

$$K(\mathcal{E}, \Delta) = \int v_i G(v_i) \sigma_{if}^{(ij)}(v_i) dv_i, \quad (5.3)$$

where  $G(v_i)$  is the distribution of the initial velocity  $v_i$ . It is assumed that the system is in thermal equilibrium. The velocity of the incoming particle,  $v_i$ , have a Maxwell-Boltzmann distribution

$$G(v_i) dv_i = 4\pi \left( \frac{\mu_i}{2\pi kT} \right)^{3/2} \exp\left(-\frac{\frac{1}{2}\mu v_i^2}{kT}\right) v_i^2 dv_i. \quad (5.4)$$

Then the rate coefficient can be written as

$$K(\mathcal{E}, \Delta) = 4\pi \left( \frac{\mu_i}{2\pi kT} \right)^{3/2} \int_{v_{i0}}^{\infty} v_i^3 \exp\left(-\frac{\frac{1}{2}\mu v_i^2}{kT}\right) \sigma_{if}^{(ij)}(v_i) dv_i. \quad (5.5)$$

One can also use the Maxwell-Boltzmann distribution of kinetic energy

$$G(E_i) = 2\sqrt{\frac{E_i}{\pi k^3 T^3}} \exp\left(-\frac{E_i}{kT}\right) \quad (5.6)$$

The corresponding rate coefficient is

$$K(\mathcal{E}, \Delta) = \left(\frac{8}{\mu_i \pi k^3 T^3}\right)^{1/2} \int_{E_{i0}}^{\infty} E_i \exp\left(-\frac{E_i}{kT}\right) \sigma_{if}^{(ij)}(E_i) dE_i. \quad (5.7)$$

## 5.2 Rate Coefficient $K(p, c)$ or $K(c, p)$

For the process

$$X(p) + M \rightarrow e^- + X^+ + M, \quad (5.8)$$

the rate coefficient can be written as

$$K(p, c) = K_0(p, c) + \frac{1}{f_z(T)} \sum_i \sum_{j \neq i} \omega_i \exp(-\epsilon_i) K((p, c)|i, j), \quad (5.9)$$

where  $K_0(p, c)$  and  $K((p, c)|i, j)$  are the rate coefficients for the elastic and inelastic collision, respectively.  $c$  indicates the continuum, and the energy is of the range from zero to infinity.

For a certain value of energy in the continuum, we write the rate coefficient as  $K(p, E_c)$  where  $E_c$  is the final kinetic energy of the free electron. The general expression of rate coefficient  $K(p, c)$  will be the integration of  $K(p, E_c)$  over  $E_c$

$$K(p, c) = \int_0^{\infty} K(p, E_c) dE_c. \quad (5.10)$$

$K(p, E_c)$  can be obtained by integrating the cross section  $\sigma_{if}^{(ij)}(p, E_c)$ , which has the same form as  $\sigma_{if}^{(ij)}(v_i)$  with just the final energy  $E_n'$  changed into  $E_c$

$$\sigma_{if}^{(ij)}(p, E_c) = \frac{2m}{M_{ij}^2 v_i^2 \pi n^3} \int_{q_{j-}}^{q_{j+}} dq_j \int_0^{r^*} r^2 dr \int_{g_m^2}^{g_+^2} \frac{(\sigma_0(g)/\omega) dg^2}{[(g_+^2 - g^2)(g^2 - g_-^2)]^{1/2}}, \quad (5.11)$$

where

$$q_{j\pm} = |\mu_i v_i \pm \sqrt{\mu_i^2 v_i^2 - 2\mu_i(E_c - E + \Delta)}|, \quad (5.12)$$

$$r^* = \frac{8mq_j^2}{m^2 q_j^4 + 2mq_j^2 \left(\frac{1}{n^2} + 2E_c\right) + 4(E_c - E)^2}, \quad (5.13)$$

$$g_m^2 = \max(g_-^2, 2\Delta/M_{ij}), \quad (5.14)$$



$$g_{\pm} = (v_i^2 + \frac{2m}{r} - \frac{m}{n^2} - 2v_i \sqrt{\frac{2m}{r} - \frac{m}{n^2}} \cos \gamma_{\pm}), \quad (5.15)$$

$$\gamma_- = |\delta - \nu| \quad \gamma_+ = \delta + \nu, \quad (5.16)$$

$$\cos \delta = \frac{2\mu_i(E_c - E + \Delta) + q_j^2}{2\mu_i v_i q_j}, \quad (5.17)$$

and

$$\cos \nu = \frac{2m(E_c - E) - q^2}{2pq} = \frac{E_c - E - mq_j^2/2}{q_j \sqrt{m(2/r - 1/n^2)}}. \quad (5.18)$$

### 5.3 Detailed Balance

Rate coefficient  $K(n, n')$  and the rate coefficient  $K(n', n)$  for the reverse process satisfy the principle of detailed balancing

$$n_E(n)K(n, n') = n_E(n')K(n', n), \quad (5.19)$$

or

$$n^2 \exp(-\epsilon_n)K(n, n') = n'^2 \exp(-\epsilon'_n)K(n', n) \quad (5.20)$$

For each term in  $K(n, n')$  we must have

$$n^2 \exp(-\epsilon_n)K_0(n, n') = n'^2 \exp(-\epsilon'_n)K_0(n', n), \quad (5.21)$$

and

$$\omega_i n^2 K(n, n' | i, j) \exp(-\epsilon_i - \epsilon_n) = \omega_j n'^2 K(n', n | j, i) \exp(-\epsilon_j - \epsilon'_n), \quad (5.22)$$

where  $\epsilon_x = E_x/k_B T$ .  $\omega_x$  is the statistic weight of level  $x$  and  $f_x(T)$  is the internal partition function. The rate coefficients are calculated by

$$K_x(n, n') = 4\pi \left(\frac{\mu_i}{2\pi kT}\right)^{3/2} \int_{v_{i0}}^{\infty} v_i^3 \exp\left(-\frac{\frac{1}{2}\mu_i v_i^2}{kT}\right) \sigma_{if}(v_i) dv_i. \quad (5.23)$$

Set the initial velocity in the reverse process is  $v_f$ , which is the final velocity of the incoming particle to the final center-of-mass of  $(j, k)$  system. We have the relation

$$\frac{1}{2}\mu_i v_i^2 - \frac{1}{2}\mu_i v_f^2 = E'_n - E_n + \Delta = \mathcal{E} + \Delta. \quad (5.24)$$

The above expression can be changed into

$$\begin{aligned}
K_x(n, n') &= \frac{4\pi\mu_i}{(2\pi kT)^{3/2}} \int_{\frac{1}{2}\mu_i v_{i0}^2}^{\infty} v_i^2 \exp\left(-\frac{\frac{1}{2}\mu_i v_f^2 - (\mathcal{E} + \Delta)}{kT}\right) \sigma_{if}(v_i) d\left(\frac{1}{2}\mu_i v_i^2\right) \quad (5.25) \\
&= \exp\left(\frac{-(\mathcal{E} + \Delta)}{kT}\right) \frac{4\pi\mu_i}{(2\pi kT)^{3/2}} \int_{\frac{1}{2}\mu_i v_{f0}^2}^{\infty} v_i^2 \exp\left(-\frac{\frac{1}{2}\mu_i v_f^2}{kT}\right) \sigma_{if}(v_i) d\left(\frac{1}{2}\mu_i v_f^2\right) \\
&= \exp(-\epsilon_j - \epsilon'_n + \epsilon_i + \epsilon_n) 4\pi \left(\frac{\mu_i}{2\pi kT}\right)^{3/2} \int_{v_{f0}}^{\infty} v_i^2 v_f \exp\left(-\frac{\frac{1}{2}\mu_i v_f^2}{kT}\right) \sigma_{if}(v_i) dv_f.
\end{aligned}$$

The rate coefficient for the reverse process is

$$K_x(n', n) = 4\pi \left(\frac{\mu_i}{2\pi kT}\right)^{3/2} \int_{v_{f0}}^{\infty} v_f^3 \exp\left(-\frac{\frac{1}{2}\mu_i v_f^2}{kT}\right) \sigma_{fi}(v_f) dv_f. \quad (5.26)$$

It is obvious that to satisfy the detailed balance equation, the cross section should also satisfy detailed balance relation

$$n^2 v_i^2 \sigma_{if}^{(ij)}(v_i) = n'^2 v_f^2 \sigma_{fi}^{(ij)}(v_f). \quad (5.27)$$

The expression of the cross section for transition  $n \rightarrow n'$  is

$$\sigma_{if}^{(ij)}(v_i) = \frac{2m}{M_{ij}^2 v_i^2 \pi n^5 n'^3} \int_{q_{j-}}^{q_{j+}} dq_j \int_0^{r^*} r^2 dr \int_{g_m^2}^{g_+^2} \frac{(\sigma_0(g)/\omega) dg^2}{[(g_+^2 - g^2)(g^2 - g_-^2)]^{1/2}}, \quad (5.28)$$

where

$$q_{j\pm} = |\mu_i v_i \pm \sqrt{\mu_i^2 v_i^2 - 2\mu_i(\mathcal{E} + \Delta)}|, \quad (5.29)$$

$$r^* = \frac{8mq_j^2}{m^2 q_j^4 + 2mq_j^2 \left(\frac{1}{n^2} + \frac{1}{n'^2}\right) + (2\mathcal{E})^2}, \quad (5.30)$$

$$g_m^2 = \max(g_-^2, 2\Delta/M_{ij}), \quad (5.31)$$

$$g_{\pm} = (v_i^2 + v_j^2 - 2v_i v_j \cos \gamma_{\pm}), \quad (5.32)$$

$$\cos \gamma_{\pm} = \cos \left( \arccos \left( -\frac{1}{v_j} \left( \frac{\mathcal{E}}{q_j} - \frac{mq_j}{2} \right) \right) \pm \arccos \left( -\frac{1}{v_i} \left( \frac{\mathcal{E} + \Delta}{q_j} + \frac{q_j}{2\mu_i} \right) \right) \right), \quad (5.33)$$

and

$$v_j = \sqrt{\frac{2m}{r} - \frac{m}{n^2}}. \quad (5.34)$$

From equation (5.24) we have

$$\mu_i v_i = \sqrt{\mu_i^2 v_f^2 + 2\mu_i(\mathcal{E} + \Delta)}, \quad (5.35)$$

$$\mu_i v_f = \sqrt{\mu_i^2 v_i^2 - 2\mu_i(\mathcal{E} + \Delta)}. \quad (5.36)$$

Thus, the limits of  $q_j$  can be written as

$$q_{j\pm} = |\mu_i v_i \pm \mu_i v_f|, \quad (5.37)$$

which are symmetric in  $v_i$  and  $v_f$ . Define

$$C = \frac{\mathcal{E} + \Delta}{q_j} + \frac{q_j}{2\mu_i}, \quad (5.38)$$

and

$$D = \frac{\mathcal{E}}{q_j} - \frac{mq_j}{2}. \quad (5.39)$$

Then  $\cos \gamma_{\pm}$  can be expressed as

$$\begin{aligned} \cos \gamma_{\pm} &= \cos \left( \arccos \left( -\frac{D}{v_j} \right) \pm \arccos \left( -\frac{C}{v_i} \right) \right) \\ &= \frac{1}{v_i v_j} (DC \mp \sqrt{(v_j^2 - D^2)(v_i^2 - C^2)}). \end{aligned} \quad (5.40)$$

We can write  $g_{\pm}^2$  as

$$\begin{aligned} g_{\pm}^2 &= v_i^2 + v_j^2 - 2v_i v_j \cos \gamma_{\pm} \\ &= v_i^2 + v_j^2 - 2(DC \mp \sqrt{(v_j^2 - D^2)(v_i^2 - C^2)}) \\ &= (\sqrt{v_j^2 - D^2} \mp \sqrt{v_i^2 - C^2})^2 + (C - D)^2. \end{aligned} \quad (5.41)$$

Define  $v_{jf}$  as the final electron velocity to the final center of mass of  $(j, k)$  system,

$$v_{jf} = \sqrt{\frac{2m}{r} - \frac{m}{n'^2}} = \frac{m}{m_j} v', \quad (5.42)$$

we have

$$\begin{aligned} v_j^2 &= \left( \frac{m}{m_j} v \right)^2 \\ &= \left( \frac{m}{m_j} \right)^2 \left( v'^2 - \frac{2\mathcal{E}}{m} \right) \\ &= v_{jf}^2 - 2m\mathcal{E}, \end{aligned} \quad (5.43)$$

where  $m_j = 1$ . We can obtain

$$\begin{aligned} v_i^2 - C^2 &= v_i^2 - \left( \frac{\mathcal{E} + \Delta}{q_j} + \frac{q_j}{2\mu_i} \right)^2 \\ &= v_f^2 + \frac{2(\mathcal{E} + \Delta)}{\mu_i} - \left( \frac{\mathcal{E} + \Delta}{q_j} + \frac{q_j}{2\mu_i} \right)^2 \\ &= v_f^2 - \left( \frac{-\mathcal{E} - \Delta}{q_j} + \frac{q_j}{2\mu_i} \right)^2, \end{aligned} \quad (5.44)$$

and

$$\begin{aligned}
v_j^2 - D^2 &= v_j^2 - \left(\frac{\mathcal{E}}{q_j} - \frac{mq_j}{2}\right)^2 \\
&= v_{jf}^2 - 2m\mathcal{E} - \left(\frac{\mathcal{E}}{q_j} - \frac{mq_j}{2}\right)^2 \\
&= v_{jf}^2 - \left(\frac{-\mathcal{E}}{q_j} - \frac{mq_j}{2}\right)^2.
\end{aligned} \tag{5.45}$$

Plug these expressions in the limits of  $g^2$ , we can get

$$\begin{aligned}
g_{\pm}^2 &= \left( \sqrt{v_{jf}^2 - \left(\frac{-\mathcal{E}}{q_j} - \frac{mq_j}{2}\right)^2} \mp \sqrt{v_f^2 - \left(\frac{-\mathcal{E} - \Delta}{q_j} + \frac{q_j}{2\mu_i}\right)^2} \right)^2 \\
&\quad + \left(\frac{\Delta}{q_j} + \frac{q_j}{2} \left(\frac{1}{\mu_i} + m\right)\right)^2.
\end{aligned} \tag{5.46}$$

Define

$$C' = \frac{-\mathcal{E} - \Delta}{q_j} + \frac{q_j}{2\mu_i}, \tag{5.47}$$

and

$$D' = \frac{-\mathcal{E}}{q_j} - \frac{mq_j}{2}, \tag{5.48}$$

which are the corresponding terms of  $C$  and  $D$  in the reverse process, where the energy  $\mathcal{E}$  and  $\Delta$  have opposite signs.  $g_{\pm}^2$  can be expressed as

$$g_{\pm}^2 = (\sqrt{v_{jf}^2 - D'^2} \mp \sqrt{v_f^2 - C'^2})^2 + \left(\frac{\Delta}{q_j}\right)^2 + \left(\frac{q_j}{2} \left(\frac{1}{\mu_i} + m\right)\right)^2 + \Delta \left(\frac{1}{\mu_i} + m\right). \tag{5.49}$$

Using the identities, (3.18) – (3.21), and  $m_j = 1$  in Hartree atomic units, we can derive the expression of the last term of  $g_{\pm}^2$  in terms of  $M_{ij}$

$$\begin{aligned}
\Delta\left(\frac{1}{\mu_i} + m\right) &= \Delta\left(\frac{m_i + m_j + m_k + m_i m_j m_k}{m_i(m_j + m_k)}\right) \\
&= \Delta\left(\frac{m_i + 1 + m_k + m_i m_k}{m_i(1 + m_k)}\right) \\
&= \Delta\left(\frac{m_i + 1}{m_i}\right) \\
&= \Delta\left(\frac{m_i + m_j}{m_i m_j}\right) \\
&= \frac{\Delta}{M_{ij}}.
\end{aligned} \tag{5.50}$$

Then  $g_{\pm}^2$  becomes

$$\begin{aligned}
g_{\pm}^2 &= (\sqrt{v_{jf}^2 - D'^2} \mp \sqrt{v_f^2 - C'^2})^2 + \left(\frac{\Delta}{q_j}\right)^2 + \left(\frac{q_j}{2}\left(\frac{1}{\mu_i} + m\right)\right)^2 + \frac{\Delta}{M_{ij}} \\
&= (\sqrt{v_{jf}^2 - D'^2} \mp \sqrt{v_f^2 - C'^2})^2 + \left(\frac{\Delta}{q_j}\right)^2 + \left(\frac{q_j}{2}\left(\frac{1}{\mu_i} + m\right)\right)^2 - \left(\frac{\Delta}{M_{ij}}\right) + \left(\frac{2\Delta}{M_{ij}}\right) \\
&= g_{\pm}^{\prime 2} + \left(\frac{2\Delta}{M_{ij}}\right).
\end{aligned} \tag{5.51}$$

Moreover we also have the detailed balance equation for the two-body differential cross section

$$g^2 \sigma_0(g) = g'^2 \sigma'_0(g'), \tag{5.52}$$

$$\sigma_0(g)/\omega = \sigma'_0(g')/\omega', \tag{5.53}$$

where  $\omega = g'/g$ . The equation (5.27) can now be proved:

$$\begin{aligned}
n^2 v_i^2 \sigma_{if}^{(ij)}(v_i) &= \frac{2m}{M_{ij}^2 \pi n^3 n'^3} \int_{q_{j-}}^{q_{j+}} dq_j \int_0^{r^*} r^2 dr \int_{g_m^2}^{g_+^2} \frac{(\sigma_0(g)/\omega) dg^2}{[(g_+^2 - g^2)(g^2 - g_-^2)]^{1/2}} \\
&= \frac{2m}{M_{ij}^2 \pi n^3 n'^3} \int_{q_{j-}}^{q_{j+}} dq_j \int_0^{r^*} r^2 dr \\
&\quad \int_{g_m^2 - \frac{2\Delta}{M_{ij}}}^{g_+^2 - \frac{2\Delta}{M_{ij}}} \frac{(\sigma'_0(g')/\omega') dg'^2}{[(g_+^{\prime 2} + \frac{2\Delta}{M_{ij}} - g'^2 - \frac{2\Delta}{M_{ij}})(g'^2 + \frac{2\Delta}{M_{ij}} - g_-^{\prime 2} - \frac{2\Delta}{M_{ij}})]^{1/2}} \\
&= \frac{2m}{M_{ij}^2 \pi n^3 n'^3} \int_{q_{j-}}^{q_{j+}} dq_j \int_0^{r^*} r^2 dr \\
&\quad \int_{g_-^{\prime 2}}^{g_+^{\prime 2}} \frac{(\sigma'_0(g')/\omega') dg'^2}{[(g_+^{\prime 2} - g'^2)(g'^2 - g_-^{\prime 2})]^{1/2}} \\
&= n'^2 v_f^2 \frac{2m}{M_{ij}^2 \pi v_f^2 n^3 n'^5} \int_{q_{j-}}^{q_{j+}} dq_j \int_0^{r^*} r^2 dr \\
&\quad \int_{g_-^{\prime 2}}^{g_+^{\prime 2}} \frac{(\sigma'_0(g')/\omega') dg'^2}{[(g_+^{\prime 2} - g'^2)(g'^2 - g_-^{\prime 2})]^{1/2}} \\
&= n'^2 v_f^2 \sigma_{fi}^{(ij)}(v_f).
\end{aligned} \tag{5.54}$$

Therefore the detailed balance relation is satisfied.

## CHAPTER VI

### RESULTS OF CROSS SECTION AND RATE COEFFICIENT

#### 6.1 *Results of Cross Sections*

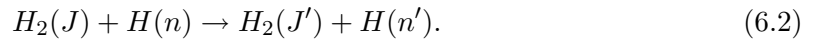
We have calculated the total cross sections for  $n - n'$ ,  $nl - n'$ , and  $nl - n'l'$  transitions for hydrogen atoms in collision with hydrogen molecules. Since there are  $n^2$  degenerated states in level  $n$ , we should take average over the initial states. The relation between different cross sections can be obtained:

$$\frac{1}{n^2}\sigma_{n,n'} = \frac{1}{n^2} \sum_l (2l+1)\sigma_{nl,n'} = \frac{1}{n^2} \sum_l (2l+1) \sum_{l'} \sigma_{nl,n'l'}, \quad (6.1)$$

where we denote the cross sections for  $n - n'$ ,  $nl - n'$  and  $nl - n'l'$  transitions as  $\sigma_{n,n'}$ ,  $\sigma_{nl,n'}$ , and  $\sigma_{nl,n'l'}$ , respectively.

##### 6.1.1 Hydrogen

We have used molecular hydrogen as the incoming particle  $i$ . The target is a hydrogen atom consisting of the electron  $j$  and the ion  $k$ . The process of  $n - n'$  transition is



We use the Hartree atomic unit for the masses (mass of the electron,  $m_j = 1$ ). The effective masses are shown in table 6.1.

The energy change of the atom is

$$\mathcal{E} = \frac{1}{2} \left( \frac{1}{n^2} - \frac{1}{n'^2} \right). \quad (6.3)$$

We have taken the Hartree energy  $E_h = 27.211\text{eV}$  as the unit of energy. In rotational

**Table 6.1:** The Effective Masses

particle	mass
$M_{ij}$	0.99973
$m$	0.99946
$\mu_i$	1224.8

excitation, the internal energy of the molecular is increased by

$$\Delta = (J'(J' + 1) - J(J + 1))B, \quad (6.4)$$

where  $B$  is the rotational constant of hydrogen molecules, ([8])

$$B = 7.35 \times 10^{-3} \text{ eV} = 2.7012 \times 10^{-4} E_h. \quad (6.5)$$

The incoming particle has the velocity  $v_i$  to the center of mass of the  $(j, k)$  system. The kinetic energy of the relative motion is

$$K_i = \frac{1}{2} \mu_i v_i^2. \quad (6.6)$$

### 6.1.2 Data Used for Differential Cross Section

The differential cross section,  $\sigma_0$  is assumed isotropic so that

$$\sigma_0 = \frac{Q}{4\pi}, \quad (6.7)$$

where  $Q$  is the total cross section for the  $e - H_2$  collision. To compare with the calculation by Flannery (1973) [8], we used the same data calculated by Henry and Lane (1969) [14]. Elastic ( $J = 0 \rightarrow 0$  and  $J = 1 \rightarrow 1$ ) and rotational cross sections ( $J = 0 \rightarrow 2$  and  $J = 1 \rightarrow 3$ ) are shown in table 6.2 and figure 6.1, where  $E_g = 1/2 M_{ij} g^2$  are the relative kinetic energy of  $e - H_2$  collision.

The  $e - H_2$  elastic scattering cross section are fitted by Flannery (1973) with

$$Q = \begin{cases} 5.7312987 - 17.07965367E_g - 20.21645021E_g^2 & E_g \leq .3 \\ 7.2192855 + 6.53604549E_g - 1.06088770E_g^2 & .3 < E_g \leq 2.5 \\ 18.24000036 + 0.08492057E_g - 0.09936507E_g^2 & 2.5 < E_g \leq 13.6. \end{cases} \quad (6.8)$$

**Table 6.2:**  $\sigma_0$ 's for elastic scattering

$E_g(eV)$	$\sigma_0(10^{-16}cm^2)$	$E_g(eV)$	$\sigma_0(10^{-16}cm^2)$
0.05	6.49	0.5	10.24
0.07	6.85	1	12.68
0.10	7.28	2.5	16.93
0.15	7.85	3.5	17.32
0.20	8.31	4.5	16.61
0.25	8.71	8	12.56
0.3	9.06		

Flannery (1973) fitted the rotational cross section  $Q$  with

$$Q = \begin{cases} -.01708813 + .3697912E_g & 0 < E_g \leq .25 \\ .04485714 + .33942857 + .22571428E_g^2 & .25 < E_g \leq 1 \\ -.531 + 1.3294E_g - .1884E_g^2 & 1 < E_g \leq 3.5 \\ 1.745 + .09260317E_g - .02082539E_g^2 & 3.5 < E_g \leq 8.16 \\ 2.6032857 - .22186974E_g + .00482343E_g^2 & 8.16 < E_g \leq 13.6 \\ 1.1 - .05606617E_g + .00075962E_g^2 & 13.6 < E_g \leq 27.2 \\ 14.97189936/E_g^{1.421023644} & E_g > 27.2. \end{cases} \quad (6.9)$$

Figure 6.1 also showed the the fitting result of (6.9).

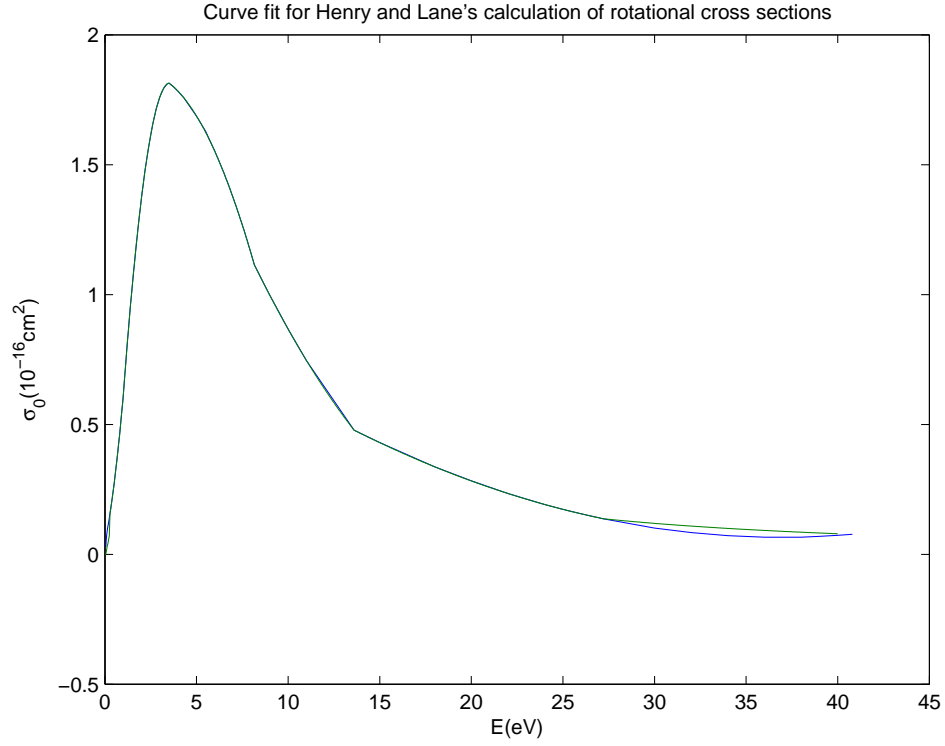
Another set of data of cross sections by Takayanagi and Geltman (1965) [15] was used for  $J = 2 \rightarrow 4$  transaction (table 6.3).

**Table 6.3:** Rotational cross section  $\sigma_0$ 's for  $J = 2, 4$ 

$E_g(eV)$	$\sigma_0(a_0^2)$
0.1029	0
0.136	0.0669
0.408	0.2305
1.36	0.8749
4.08	3.415

The cross sections by Takayanagi and Geltman (1965) [15] are fitted by Flannery (1973) [8]





**Figure 6.1:** Flannery's fitting results for rotational cross section of  $e - H_2$  collision.

with

$$Q = \begin{cases} 0.1356068335 * (1 - 0.1029/E)^{1/2} E_g & 0.1029 < E_g \leq .136, \\ -.01148059 + .56795051 E_g + .06161778 E_g^2 & .136 < E_g \leq 1.36, \\ -.9250381 + 1.45334442 E_g - .09549340 E_g^2 & 1.36 < E_g \leq 13.6. \end{cases} \quad (6.10)$$

### 6.1.3 Results for Transition $n \rightarrow n'$

We used (6.7) and the fitted data (6.8–6.10) for the two-body differential cross sections. The results of total cross section  $\sigma(n)$  for transition ( $n' = n - 1$  and  $J' = 0, 2$ ) are listed in table 6.4. The unit for the cross section is  $a_0^2$ . The corresponding process is

$$H_2(J = 0) + H(n) \rightarrow H_2(J' = 0, 2) + H(n - 1). \quad (6.11)$$

The initial kinetic energy of the relative motion is give by  $\epsilon$

$$K_i = \epsilon * 0.0215 \text{ eV}. \quad (6.12)$$

The ratio of the results  $\sigma(n)$  to the data  $\sigma^F$  calculated by Flannery(1973) [8] are also listed. Elastic results ( $J' = J$ ) are labeled as  $\sigma(ne)$ . The results showed that the cross section calculated by the quantum impulse approximation matched well with the binary encounter results.

**Table 6.4:** Cross sections for the Process  $H_2(J = 0) + H(n) \rightarrow H_2(J' = 0, 2) + H(n - 1)$

$\epsilon$	$\sigma(10)$	$\sigma/\sigma^F$	$\sigma(9)$	$\sigma/\sigma^F$	$\sigma(9e)$	$\sigma/\sigma^F$	$\sigma(8)$	$\sigma/\sigma^F$
0.001	0	0	40172	0.89072	2.6552	0.46017	81.691	1.0023
0.01	0	0	11073	0.87882	1.0163	0.49337	27.584	1.0104
0.05	0	0	3484.6	0.85616	0.86215	0.57096	15.78	1.0051
0.1	0	0	1936	0.85289	1.0184	0.65702	14.261	0.99728
0.6	1.1683	1.0159	365.26	0.84747	2.7426	0.92033	18.439	0.95539
1	6.4343	0.99295	222.04	0.85072	4.0619	0.95798	20.695	0.98549
2.5	9.9953	0.97042	89.767	0.85492	8.9005	0.99893	22.119	0.98306
5	9.1564	0.94983	44.999	0.85225	15.821	1.0077	19.972	0.97424
10	6.8703	0.90877	22.523	0.85316	25.835	0.99747	15.803	0.96361
30	3.3332	0.85248	7.5195	0.85255	42.702	1.0649	8.4422	0.93181
50	2.2216	0.83519	4.5177	0.85239	46.141	1.3221	5.7959	0.91708
80	1.4934	0.82508	2.829	0.85211	44.653	1.5292	3.9681	0.90596
100	1.0792	0.72432	2.3634	0.88848	28.767	1.0774	3.0722	0.84171

Table 6.5 is the cross section  $\sigma(n)$  for processes

$$H_2(J = 1) + H(n) \rightarrow H_2(J' = 1, 3) + H(n - 3). \quad (6.13)$$

Table 6.6 is the cross section for processes

$$H_2(J = 2) + H(n) \rightarrow H_2(J' = 2, 4) + H(n - 3). \quad (6.14)$$

#### 6.1.4 Results for Transition $nl \rightarrow n'$ and $nl \rightarrow n'l'$

Consider the process

$$H_2(J = 2) + H(7) \rightarrow H_2(J = 4) + H(6), \quad (6.15)$$

**Table 6.5:** Cross sections  $\sigma(n)$  for the Process  $H_2(J=1)+H(n) \rightarrow H_2(J'=1,3)+H(n-3)$ 

$\epsilon$	$\sigma(13)$	$\sigma/\sigma^F$	$\sigma(12)^F$	$\sigma/\sigma^F$	$\sigma(12e)^F$	$\sigma/\sigma^F$	$\sigma(11)$	$\sigma/\sigma^F$
0.001	0	0	11247	N/A	0.033561	N/A	4.1298	1.6454
0.01	0	0	5305.1	0.64382	0.011106	N/A	1.4014	1.6565
0.05	0	0	1250.2	0.70236	0.0057929	N/A	0.81477	1.6939
0.5	0	0	127.28	0.71105	0.0098104	0.51096	1.0661	1.6555
1	0.14682	1.6837	63.653	0.7112	0.031467	0.7024	1.4615	1.6458
2.5	0.88935	1.6654	25.469	0.71144	0.12286	0.91687	2.0422	1.647
5	1.1512	1.6661	12.739	0.71167	0.30113	0.97768	2.2437	1.6498
10	1.1636	0.98611	6.3724	0.7112	0.6751	0.99866	2.1583	1.635
30	0.81325	0.70108	2.1272	0.71145	1.8668	0.99829	1.5452	0.91977
50	0.60574	0.69866	1.2781	0.71003	2.6792	0.99971	1.174	0.8326
80	0.4381	0.70096	0.80042	0.70833	3.4654	1.0696	0.86017	0.80389
100	0.37033	0.70005	0.64119	0.71085	3.8062	1.2007	0.72996	0.79343

**Table 6.6:** Cross sections for the Process  $H_2(J=2)+H(n) \rightarrow H_2(J'=2,4)+H(n-1)$ 

$\epsilon$	$\sigma(8)$	$\sigma/\sigma^F$	$\sigma(7)$	$\sigma/\sigma^F$	$\sigma(7e)$	$\sigma/\sigma^F$	$\sigma(6)$	$\sigma/\sigma^F$
0.15	0	0	453.46	1.0077	0.020119	N/A	0.68074	3.1371
0.2	0	0	527.55	0.96798	0.026021	N/A	0.68447	2.2892
0.6	0	0	299.39	0.9045	0.054016	8.7688	1.2705	1.1764
0.8	0	0	239.19	0.89584	0.065138	1.0802	1.6069	1.1006
1	0	0	199.12	0.88893	0.080582	0.57973	1.9293	1.0659
2.5	0.46218	1.0158	88.862	0.8712	0.6255	0.69346	3.7884	1.0049
5	1.4614	0.98743	46.499	0.87077	2.3205	0.89942	5.4672	0.99223
10	1.8826	0.97544	23.84	0.87007	6.3691	0.97686	6.5707	0.83597
30	1.5921	0.93653	8.0712	0.87068	20.219	1.0059	5.7985	0.96965
50	1.2596	0.91275	4.856	0.87025	28.354	0.99838	4.753	0.96215
80	0.95194	0.88966	3.041	0.87135	34.692	0.99977	3.6994	0.951
100	0.8191	0.88075	2.4352	0.87283	36.788	0.99967	3.2202	0.94712

with the initial kinetic energy as  $0.0215eV$ , and the data by Henry and Lane (1969) [14]

fitted with (6.10), from table 6.6 we know that

$$\sigma_{7,6} = 199.12 \quad a_0^2. \quad (6.16)$$

The corresponding cross sections for the initial states with different  $l'$ s are shown in table 6.7.

The cross sections of  $\sigma_{7l,6l'}$  are shown in table 6.8.

**Table 6.7:** Cross sections  $\sigma_{7l,6}$ 

$l$	0	1	2	3	4	5	6
$\sigma_{7l,6}$	167.02	254.89	271.04	257.72	223.91	187.28	170.59
$(2l+1)\sigma_{7l,6}$	167.02	764.67	1355.2	1804.1	2015.2	2060.1	2217.7

**Table 6.8:** Cross sections  $\sigma_{7l,6l'}$ 

$l \backslash l'$	0	1	2	3	4	5	$\sum_{l'} \sigma_{7l,6l'}$
0	8.2339	26.558	42.33	44.276	38.304	32.912	192.61
1	26.38	95.384	145.66	139.86	120.97	102.24	630.48
2	41.687	144.28	549.92	276.36	219.35	184.15	1415.7
3	41.585	135.87	279.84	807.25	364.67	294.32	1923.5
4	37.013	118.43	220.45	385.84	821.38	461.53	2044.6
5	34.973	109.55	194.53	305.92	499.99	829.76	1974.7
6	43.556	134.46	240.21	355.22	485.29	801.99	2060.7

We can get

$$\frac{1}{7^2} \sum_l (2l+1) \sigma_{7l,6} = 211.92 \quad a_0^2, \quad (6.17)$$

and

$$\frac{1}{7^2} \sum_l \sum_{l'} \sigma_{7l,6l'} = 209.03 \quad a_0^2. \quad (6.18)$$

Thus the relation between different cross sections, equation (6.1), is satisfied.

## 6.2 Results for Rate Coefficients

Once we get the cross sections, rate coefficients can be obtained by integrating the cross section over the velocity of the incoming particles,  $v_i$ . The cross sections for electron-molecule collisions are given recent experimental data and calculation results. The data we have chosen are in the low energy region ( $0-10\text{eV}$ ) that fits our low temperature condition. We only considered several lower level transitions such as  $0 \rightarrow 2$ ,  $1 \rightarrow 3$  in rotation and  $0 \rightarrow 1$  in vibration. Transitions to higher levels are ignored for larger energy gap and little possibility. Those data were also fitted segment by segment with quadratic functions.

### 6.2.1 Rotation and Vibration Levels of the Incoming Molecule

The internal energy levels of a molecule are generally expressed as the sum of energies due to rotation and vibration

$$E(v, J) = E_{vib} + E_{rot}. \quad (6.19)$$

The rotational energy  $E_{rot}$  is

$$E_{rot}/hc = BJ(J+1), \quad (6.20)$$

where  $B$  is the rotational constant. The vibrational energy  $E_{vib}$  of a molecular can be approximately treated as the levels of a simple harmonic vibrator

$$E_{vib}/hc = E_v(\nu + 1/2), \quad (6.21)$$

where  $E_v$  is the vibrational constant. The constants of  $E_v$  and  $B$  of molecules  $H_2$ ,  $N_2$ ,  $O_2$ ,  $CO$ ,  $H_2O$ , and  $CO_2$  are given by Itikawa (2007) [16].

Table 6.9 shows the rotational constants  $B$  and the vibrational constants  $E_v$  of molecules  $H_2$ ,  $N_2$ ,  $O_2$ , and  $CO$ .

**Table 6.9:** Rotational and vibrational constants

M	$B_\nu$	$E_v$
	<i>a.u.</i>	<i>a.u.</i>
$H_2$	2.703-4*	1.89486-2
$N_2$	9.06566-6	1.0616483-2
$O_2$	6.551-6	7.091-3
$CO$	8.76-6	9.765772-3

\*2.703 - 4 =  $2.703 \times 10^{-4}$

Table 6.10 shows the rotational and the vibrational constants  $B$  and  $E_v$  of molecules  $H_2O$ .

Table 6.11 shows the vibrational constants  $E_v$  of molecules  $CO_2$ .

## 6.2.2 Differential Cross Sections of the Incoming Molecule

**Table 6.10:** vibrational and rotational constants of  $H_2O$ 

State	$E_v$ <i>eV</i>	$E_v$ <i>a.u.</i>	$J_\tau$	$B$ <i>meV</i>	$B$ <i>a.u.</i>
000	0	0	0 <sub>0</sub>	0.0	0.0
010	0.1977	.007266	1 <sub>0</sub>	4.604	.0001692
-	-	-	2 <sub>-2</sub>	8.69	-
100	0.4534	.016889	2 <sub>0</sub>	11.8	0.00043366
-	-	-	2 <sub>2</sub>	16.882	-
-	-	-	3 <sub>-2</sub>	17.64	-
001	0.4657	.016889	3 <sub>0</sub>	25.578	0.00094
-	-	-	3 <sub>2</sub>	35.363	-

**Table 6.11:** The vibrational constants of  $CO_2$ 

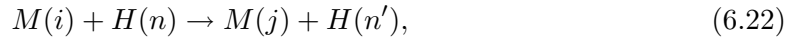
State	$E_v$ <i>cm<sup>-1</sup></i>	$E_v$ <i>a.u.</i>
000	0	0
010	667.4	.00304
100	1388	.00632
001	2349	0.0107

Many data of two-body differential cross sections are collected by Brunger, et al., (2002) [17] and Itikawa, et al., (2005) [18]. The elastic cross sections for  $e - H_2$  scattering are given by Brunger, et al., (1991) [19]. England et al. (1988) [20] reported the swarm-derived rotational and vibrational cross sections for  $e - H_2$  scattering. Onda (1995) [21] calculated the elastic and rotational cross sections for  $e - N_2$  scattering. The vibrational cross sections of  $e - N_2$  scattering are given by Feng, et al., (2003) [22]. The elastic, rotational and vibrational cross sections for  $e - CO_2$  and  $e - H_2O$  scattering are given by Itikawa (2001), and Itikawa, et al., (2004) [23] [24]. Kanik, et al., (1993) [25], Bhattacharyya, et al., (1983) [26], and Noble et al. (1996) [27] gave the elastic, rotational and vibrational cross sections for  $e - O_2$  scattering, respectively. The elastic cross sections for  $e - CO$  scattering are provided by Kanik, et al., (1992) [28]. The rotational cross sections for  $e - CO$  scattering are given by Randell, et al., (1996) [29]. The vibrational cross sections for  $e - CO$  scattering are given by Gibson, et al., (1996) [30].

### 6.3 *Results of the Resonant Effect for the Inelastic Rate Coefficients*

We have calculated the inelastic rate coefficients for the common gases in the air:  $H_2$ ,  $N_2$ ,  $O_2$ ,  $CO$ ,  $CO_2$ , and  $H_2O$ . Resonant transitions ( $n \rightarrow n'$ ) and their neighbor transitions have been chosen with energy changes that are close to the internal energy change of the molecule. Results are shown in tables below. The first three columns are the initial and final energy levels for the electron and the molecule. The next three columns are the energy changes of the electron and the molecule and the combined energy change. The last column shows the rate coefficients  $K(n, n'|i, j)$  calculated in the units of  $cm^3/s$ . These results show that two major factors are affecting the results. For the combined energy change is close to zero, we see the resonant effect that the rate coefficient is much larger than the neighbor transitions. For high levels, the energy gaps become smaller and the width of the levels are thinner. The rate coefficients are getting smaller as  $n$  increases and the resonant effect is possibly eliminated.

The corresponding processes are



where  $M$  denotes the molecule with level  $i$  for the initial internal energy level  $(J, \nu)$  or level  $j$  for the final level  $(J', \nu')$ .

Table 6.12 shows the results of rate coefficients for  $e - H_2$  scattering, and results for other gases,  $N_2$ ,  $O_2$ ,  $CO$ ,  $CO_2$ , and  $H_2O$  are shown in table 6.13 – 6.17, respectively

**Table 6.12:** Rate coefficients of electron recombined with  $H^+$  by colliding with incoming  $H_2$  molecule

$n - n'$	$J - J'$	$\nu - \nu'$	$\mathcal{E}$	$\Delta$	$(\mathcal{E} + \Delta)$	rate( $k$ )
			<i>a.u.</i>	<i>a.u.</i>	<i>a.u.</i>	$cm^3/s$
9-8	0-0	0-0	-1.6397-3*	0.0	-1.6397-3	4.017-11
8-7	0-2	0-0	-2.39-3	1.6217-3	-7.6985-4	4.89-11
9-8	0-2	0-0	-1.6397-3	1.6217-3	1.7954-05	1.451-9
10-9	0-2	0-0	-1.17-3	1.6217-3	4.4895-4	3.435-11
11-8	1-3	0-0	-3.68-3	2.70-3	-1.02-3	1.37-12
12-9	1-3	0-0	-2.7-3	2.70-3	2.30-6	2.233-10
13-10	1-3	0-0	-2.041-3	2.70-3	6.6-4	1.013-12
6-4	0-0	0-1	-1.7361-2	0.01894	1.5867-3	5.98-8
7-4	0-0	0-1	-2.1046-2	0.01894	-2.0983-3	5.067-8
7-5	0-0	0-1	-9.7959-3	0.01894	9.1518-3	1.022-27

$$* - 1.6397 - 3 = -1.6397 \times 10^{-3}$$

**Table 6.13:** Rate coefficients of electron recombined with  $H^+$  by colliding with incoming  $N_2$  molecule

$n - n'$	$J - J'$	$\nu - \nu'$	$\mathcal{E}$	$\Delta$	$(\mathcal{E} + \Delta)$	rate( $k$ )
			<i>a.u.</i>	<i>a.u.</i>	<i>a.u.</i>	$cm^3/s$
20-18	0-0	0-0	-2.93-4	0.0	-2.93-4	3.887-11
66-54	0-0	0-0	-5.668-5	0.0	-5.668-5	1.38-12
18-16	0-2	0-0	-4.0992-4	5.439-5	-3.555-4	4.19-12
42-38	0-2	0-0	-6.28-5	5.439-5	-8.42-6	1.383-11
43-39	0-2	0-0	-5.8315-5	5.439-5	-3.92-6	1.097-11
44-40	0-2	0-0	-5.42-5	5.439-5	1.58-7	1.04-11
45-41	0-2	0-0	-5.05-5	5.439-5	3.86-6	8.30-12
66-54	0-2	0-0	-5.668-5	5.439-5	2.29-6	9.7-13
26-23	0-4	0-0	-2.055-4	1.813-4	-2.422-5	3.77-11
27-24	0-4	0-0	-1.8218-4	1.813-4	-8.713-7	4.28-11
28-25	0-4	0-0	-1.622-4	1.813-4	1.9068-5	2.558-11
12 - 6	0-0	0-1	-1.0417-2	0.0106	1.99-4	9.266-011
13 - 6	0-0	0-1	-1.093-2	0.0106	-3.135-4	6.092-11
14 - 6	0-0	0-1	-1.1338-2	0.0106	-7.215-4	1.240-11



**Table 6.14:** Rate coefficients of electron recombined with  $H^+$  by colliding with incoming  $O_2$  molecule

$n - n'$	$J - J'$	$\nu - \nu'$	$\mathcal{E}$	$\Delta$	$(\mathcal{E} + \Delta)$	rate( $k$ )
			<i>a.u.</i>	<i>a.u.</i>	<i>a.u.</i>	$cm^3/s$
10-9	0-0	0-0	-1.17-3	0.0	-1.17-3	2.34-11
44-39	1-3	0-0	-7.047-5	6.55-05	-4.96-6	1.0898-19
45-40	1-3	0-0	-6.56-5	6.55-05	-7.76-8	8.988-19
46-41	1-3	0-0	-6.11-5	6.55-05	4.36-6	7.454-19
9-6	0-0	0-1	-7.716-3	7.091-3	-6.25-4	2.1656-8
11-7	0-0	0-1	-6.072-3	7.091-3	1.019-3	9.19-10
12-7	0-0	0-1	-6.73-3	7.091-3	3.59-4	2.769-9
26-8	0-0	0-1	-7.0729-3	7.091-3	1.821-5	8.0922-11

**Table 6.15:** Rate coefficients of electron recombined with  $H^+$  by colliding with incoming  $CO$  molecule

$n - n'$	$J - J'$	$\nu - \nu'$	$\mathcal{E}$	$\Delta$	$(\mathcal{E} + \Delta)$	rate( $k$ )
			<i>a.u.</i>	<i>a.u.</i>	<i>a.u.</i>	$cm^3/s$
10-9	0-0	0-0	-1.1728-3	0.0	-1.1728-3	6.745-11
20-18	0-0	0-0	-2.93-4	0.0	-2.93-4	1.829-11
20-18	0-1	0-0	-2.93-4	1.752-5	-2.7569-4	3.08-12
38-37	0-1	0-0	-1.897-5	1.752-5	-1.449-6	2.32-14
39-38	0-1	0-0	-1.7529-5	1.752-5	-9.0256-9	1.90-14
40-39	0-1	0-0	-1.623-5	1.752-5	1.289-6	1.55-14
29-28	1-2	0-0	-4.32-5	3.504-5	-8.18-6	1.015-13
30-29	1-2	0-0	-3.898-5	3.504-5	-3.93-6	7.86-14
31-30	1-2	0-0	-3.526-5	3.504-5	-2.237-7	6.139-14
32-31	1-2	0-0	-3.20-5	3.504-5	3.03-6	4.587-14
10-6	0-0	0-1	-8.89-3	9.766-3	8.77e-4	2.04-11
11-6	0-0	0-1	-9.757-3	9.766-3	9.11-6	5.75-10
12-6	0-0	0-1	-1.04-2	9.766-3	-6.509-4	6.069-11

**Table 6.16:** Rate coefficients of electron recombined with  $H^+$  by colliding with incoming  $H_2O$  molecule

$n - n'$	$J - J'$	$\nu - \nu'$	$\mathcal{E}$	$\Delta$	$(\mathcal{E} + \Delta)$	rate( $k$ )
			<i>a.u.</i>	<i>a.u.</i>	<i>a.u.</i>	$cm^3/s$
10-9	0-0	0-0	-1.1728-3	0.0	-1.1728-3	6.69-12
23-21	0-1	0-0	-1.886-4	1.692-4	-1.94-5	8.23-7
24-22	0-1	0-0	-1.65-4	1.692-4	4.20-6	1.218-6
25-23	0-1	0-0	-1.45-4	1.692-4	-2.40-5	5.19-7
22-18	0-2	0-0	-5.10-4	4.337-4	-7.649-5	3.57-9
23-19	0-2	0-0	-4.399-4	4.337-4	-6.198-6	2.14-8
24-20	0-2	0-0	-3.819-4	4.337-4	5.17-5	4.92-9
13-11	0-3	0-0	-1.17-3	9.40-4	-2.336-4	3.19-10
14-12	0-3	0-0	-9.21-04	9.40-4	1.88-5	1.27-8
15-13	0-3	0-0	-7.36-4	9.40-4	2.037-4	1.88-10
14-7	0-0	000-010	-7.65-3	7.265-3	-3.87-4	4.627-11
13-7	0-0	000-010	-7.25-3	7.265-3	2.02-5	1.23-9
12-8	0-0	000-010	-4.34-3	7.265-3	2.93-3	1.11-16
5-4	0-0	000-001/100	-1.125-2	.01689	5.639-3	8.64-18
6-4	0-0	000-001/100	-1.736-2	.01689	-4.72-4	1.84-9
7-4	0-0	000-001/100	-2.10-2	.01689	-4.157-3	5.65-14

**Table 6.17:** Rate coefficients of electron recombined with  $H^+$  by colliding with incoming  $CO_2$  molecule

$n - n'$	$J - J'$	$\nu - \nu'$	$\mathcal{E}$	$\Delta$	$(\mathcal{E} + \Delta)$	rate( $k$ )
			<i>a.u.</i>	<i>a.u.</i>	<i>a.u.</i>	$cm^3/s$
10-9	0-0	0-0	-1.1728-3	0.0	-1.1728-3	2.20-11
15-10	0-0	000-010	-2.78-3	3.04-3	2.63-4	1.75-12
16-10	0-0	000-010	-3.047-3	3.04-3	-5.82-6	2.85-12
17-10	0-0	000-010	-3.27-3	3.04-3	-2.288-4	1.41-12
17-8	0-0	000-100	-6.082-3	6.32-3	2.42-4	1.725-12
18-8	0-0	000-100	-6.269-3	6.32-3	5.52-5	2.398-12
19-8	0-0	000-100	-6.428-3	6.32-3	-1.029-4	1.797-12
11-6	0-0	000-001	-9.757-3	1.07-2	9.467-4	1.38-12
12-6	0-0	000-001	-1.04-2	1.07-2	2.867-4	1.69-11
13-6	0-0	000-001	-1.09-2	1.07-2	-2.269-4	1.91-11
14-6	0-0	000-001	-1.13-2	1.07-2	-6.34-4	4.14-12

## CHAPTER VII

### RECOMBINATION COEFFICIENT

Recombination coefficients are calculated in terms of rates coefficients. Similar assumptions are made as in Bates' previous work [3] [4] that it is in dense plasmas and the distribution among the degenerate states in one level is uniform. Collisions mostly happen between the electrons and the incoming particles. As defined in previous chapters,  $n(p)$  is the number density of the excited state  $p$ ,  $n_e$  is the number density of free electron,  $n(N^+)$  is the number density of the ion, and  $N$  is the number density of the incoming particle. The radiative recombination term was initially added and then dropped for its very little contribution. The number densities of free particle and the ion are assumed much larger than the number densities of the excited states. Thus a quasi-equilibrium condition can be established very rapidly. A set of quasi-equilibrium equations are established to solve the number density distribution and the sum of the rates of the transitions into the sink are calculated to obtain the recombination coefficient.

#### *7.1 The Quasi-Equilibrium Equations*

In the quasi-equilibrium condition, number densities of atoms in level  $p$  are not changing. We can write the similar quasi-equilibrium equations as those given by Bates (1962) [3]. As defined in (3, 8)

$$\rho(p) = n(p)/n_E(p), \quad (7.1)$$

where  $n_E(p)$  is the number density of the excited state  $p$  of the atom in Saha equilibrium. There are infinite equations of quasi-equilibrium for the infinite levels of the electron. However, for the levels that are high enough,  $\rho(p)$  will be very close to unity. We can just consider the equations below a certain level  $s$  and set the  $\rho's$  for higher levels as 1. For the

boundary of the sink, level  $u$ , we can set it at where the energy level is low enough and  $\rho(u)$  is close to zero. Thus, by solving the finite number of equations, from level  $u$  to  $s$ , we can get the number density distribution  $\rho(p)$

$$\begin{aligned}\rho(p)\mathcal{K}(p) &= \sum_{m \neq p}^s \rho(m) \frac{n_E(m)}{n_E(p)} K(m, p) + \sum_{m > p}^s \rho(m) \frac{n_E(m)}{n_E(p)N} A(m, p) \\ &+ \sum_{m=p+1}^{\infty} \frac{n_E(m)}{n_E(p)} \left( K(m, p) + \frac{A(m, p)}{N} \right) + K(p, c),\end{aligned}\quad (7.2)$$

where

$$\mathcal{K}(p) = K(p, c) + \sum_{m \neq p} K(p, m) + \frac{1}{N} \sum_{m < p} A(p, m), \quad (7.3)$$

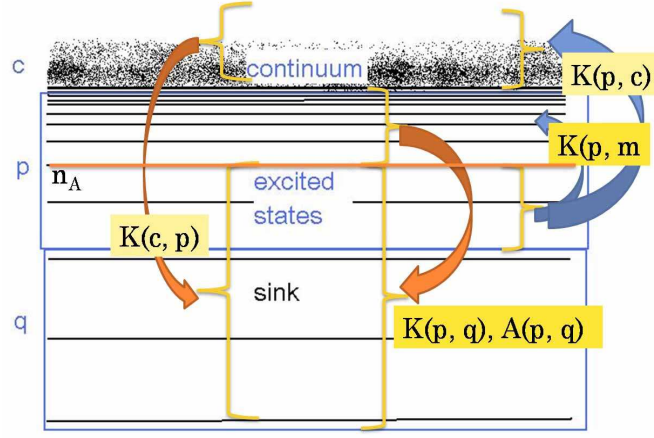
$$\frac{n_E(m)}{n_E(p)} = \frac{m^2}{p^2} \exp(157890(p^2 - m^2)/(p^2 m^2 T)). \quad (7.4)$$

## 7.2 Derivation of Rate through Level $n_A$

When calculating the quasi-equilibrium equations, we realized that it was hard to make a good choice for  $u$ . The results could be unstable and a single calculation from the equation by Bates (1981) [9] may not represent the recombination coefficient correctly. Therefore we tried to find the rate flow passing through a level  $n_A$  between  $u$  and  $s$ . Define a new rate by summing over all the transitions passing downwards through  $n_A$  and subtracting all those transitions passing upwards through it (figure 7.1). As the quasi-equilibrium is established, the rate flow through each level between  $u$  and  $s$  should be the same. The equations for solving the rate flow through all the levels can be written as:

$$\begin{aligned}\alpha &= \frac{1}{n_e N^+} \sum_{q=1}^{n_A-1} \left( \sum_{p=n_A}^s n_E(p) \rho(p) \left( K(p, q) + \frac{A(p, q)}{N} \right) \right. \\ &+ \sum_{p=s+1}^{\infty} n_E(p) \left( K(p, q) + \frac{A(p, q)}{N} \right) \\ &+ n_E(q) K(q, c) \left. \right) \\ &- \sum_{q=u}^{n_A-1} n_E(q) \rho(q) \left( \sum_{p=na}^{\infty} K(q, p) + K(q, c) \right).\end{aligned}\quad (7.5)$$

When  $n_A$  is set to be  $u$ , the equation (7.5) can be reduced to Bates' equation for combination



**Figure 7.1:** Transitions passing through level  $n_A$ .

coefficient,

$$\begin{aligned} \alpha = & \frac{1}{n_e N^+} \sum_{q < u} \left( \sum_{p=u}^s n_E(p) \rho(p) \left( K(p, q) + \frac{A(p, q)}{N} \right) \right. \\ & + \sum_{p=s+1}^{\infty} n_E(p) \left( K(p, q) + \frac{A(p, q)}{N} \right) \\ & \left. + n_E(q) K(q, c) \right), \end{aligned} \quad (7.6)$$

where the last two terms are very small and ignorable.

### 7.2.1 The Transition Rates $A(p, m)$

The data of  $k(p, m)$  and  $K(p, c)$  has been calculated up to  $p, m = 100$ . The old way of calculating the Einstein spontaneous transition probability  $A(p, m)$  [30] will fail on most computers since the factorial function of larger argument will simply overflow. Flannery, et al., (2003) [31] have given a approximation

$$\begin{aligned} A &= \frac{1}{n_i^2} \left( \sum_{l=1}^{n_f-1} A_{n_i, l-1 \rightarrow n_f, l} + \sum_{l=0}^{n_f-1} A_{n_i, l+1 \rightarrow n_f, l} \right) \quad (7.7) \\ A_{n_i, l_i \rightarrow n_f, l_f} &= \frac{4A_0}{3} \frac{l_{>}}{2l_i + 1} \left( \frac{n_i^2 - n_f^2}{2n_i^2 n_f^2} \right)^2 |R_{ki}(i, n_i, l_i, \Delta l)| |R_{ki}(f, n_i, l_i, \Delta l)| \\ R_{ki}(j, n_j, l_j, \Delta l) &= \frac{n_j^2}{2k_j} \left[ \left( 1 - \Delta l \frac{l_j}{n_j} \right) J_{k_j-1}(k_j \epsilon_j) - \left( 1 + \Delta l \frac{l_j}{n_j} \right) J_{k_j+1}(k_j \epsilon_j) \right], \end{aligned}$$

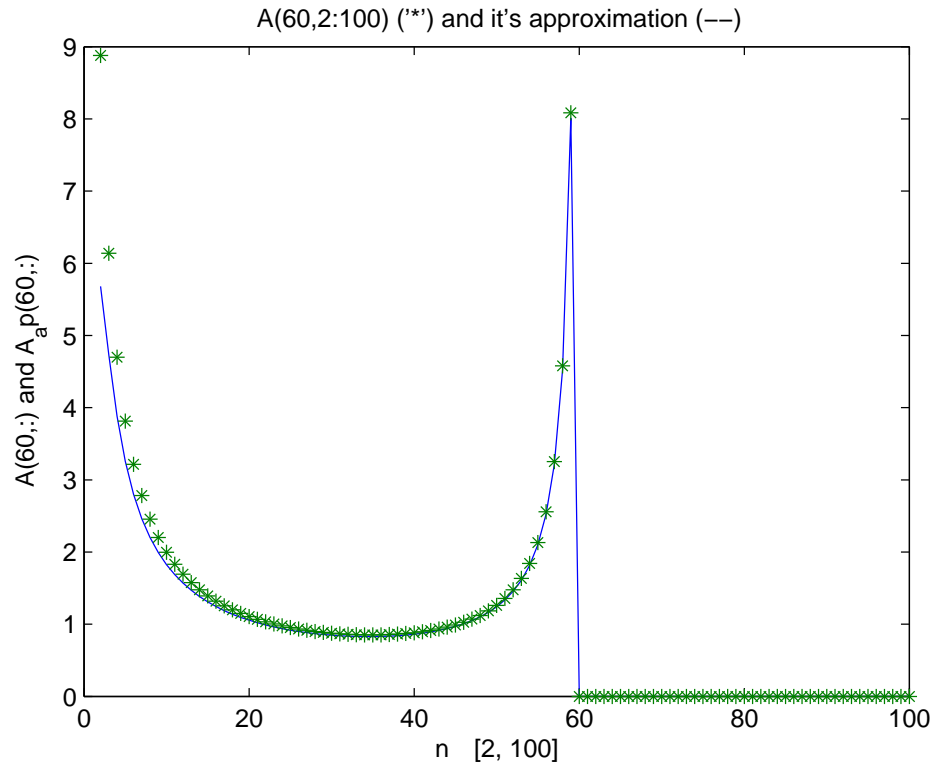
where

$$\epsilon_j = (1 - (l_i + 1/2)^2/n_j^2)^{1/2}, \quad \Delta l = l_f - l_i, \quad (7.8)$$

and

$$A_0 = 1.606501 \times 10^{10} \quad l_{>} = \max(l_f, l_i). \quad (7.9)$$

This approximation has been used to calculate  $A(p, m)$  up to  $p = 100$ . Comparison is shown in figure 7.2 between the original results and the new approximation of  $A(60, 2 : 100)$ . It shows that they make an excellent agreement.



**Figure 7.2:** The new approximation of  $A(60, 2 : 100)$ .

### 7.3 Scattering Amplitude

In the equation of the cross section, the scattering amplitude is defined as,

$$|f_{if}|^2 = \sigma_0(g), \quad (7.10)$$

which only holds when the collision is elastic.  $\sigma_0(g)$  is the differential cross section of the two-body collision of the electron and the incoming molecules, and  $g$  is the initial relative speed. For inelastic collision, the scattering amplitude is

$$\sigma_0(g) = \frac{g'}{g} |f_{if}|^2 = \omega |f_{if}|^2, \quad (7.11)$$

where  $g'$  is the relative speed after the collision and  $\omega = g'/g$ . The experimental data we have collected are the total cross section  $Q(g)$  with the excitation of the molecular internal energy. Assuming that the collision is isotropic, the differential cross section are calculated by:

$$\sigma_0(g) = \frac{Q(g)}{4\pi}. \quad (7.12)$$

So the scattering amplitude is

$$|f_{ij}|^2 = \frac{Q(g)}{4\pi\omega}. \quad (7.13)$$

For the deexcitation collision, the cross section's data are not given. We can obtain the scattering amplitude from the reverse process cross section  $\sigma_{if}(g')$  using the detailed balancing principle,

$$g^2 \sigma_0(g) = (g')^2 \sigma_0(g'), \quad (7.14)$$

where  $g_i$  and  $g_f$  are the degeneration of the internal energy level of the molecule. We have

$$\sigma_0(g) = \frac{g^2}{g'^2} \sigma_0(g'). \quad (7.15)$$

Therefore the expression in the cross section equation (4.94),  $\sigma_0(g)/\omega$ , will be replaced by

$$\frac{\sigma_0(g)}{\omega} = \frac{g^2}{g'^2} \frac{\sigma_0(g')}{\omega} = \sigma_0(g') * \omega \quad (7.16)$$

## 7.4 *Byron Bottleneck Check*

Among the excited levels, there exist a Byron bottleneck level, where the number densities has the minimum in equilibrium. One can assume that all levels higher than the bottleneck level are in the Saha equilibrium, and all the levels bellow are empty. Thus we can calculate all the downward rates flow passing through the bottleneck level to get an

upper limits of the combination coefficient, which helps us to determine the order of the combination coefficient. When the temperature is  $250K$  for hydrogen atoms, the bottle-neck of Byron, et al., (1962) [33] is about  $n^* = 25$  at where  $n_E(p)$  is the minimum and  $dn_E(p)/dp = 0$ . Since,

$$\frac{n_E(p)}{n_e N^+} = p^2 (h^2/2\pi k_B T)^{3/2} \exp(I_p/kT) = 4.2 \times 10^{-16} (p^2/T^{3/2}) \exp(157890/p^2 T), \quad (7.17)$$

at  $p = n^*$ , we have

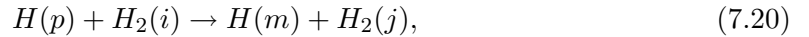
$$\begin{aligned} \frac{dn_E(p)}{dp} &= \frac{4.2 \times 10^{-16}}{T^{3/2}} \exp\left(\frac{157890}{p^2 T}\right) (2p + p^2 \frac{157890}{T} (-2p^{-3})) = 0 \\ n^* &= \frac{157890}{T n^*} \\ n^* &= 25.131|_{T=250K}. \end{aligned} \quad (7.18)$$

The rate passing Byron bottleneck can be obtained by

$$\alpha_b = \sum_{q=n^*}^{\inf} \rho(q) \left( 4.2 \times 10^{-16} \frac{q^2}{T^{3/2}} \exp\left(\frac{157890}{q^2 T}\right) \sum_{p=1}^{n^*-1} \left( K(q, p) + \frac{A(q, p)}{N} \right) \right). \quad (7.19)$$

## 7.5 Rate Coefficient of $H_2$

We take hydrogen nucleus as the ion and hydrogen molecule as the incoming particle and write down the expression of rate coefficient as an example. For process



three lowest excitations/deexcitations have been counted in the internal energy change for the  $H_2$  molecule. It can be rotational excited from  $J = 0$  to  $J = 2$  and from  $J = 1$  to  $J = 3$  and vibrational excited from  $v = 0$  to  $v = 1$ . The rate coefficients  $K(p, m)$  is calculated by

$$\begin{aligned} K(p, m) &= K_0(p, m) \\ &+ \frac{1}{f_B(T)} \left( K(p, m|0, 2) + 3 \exp\left(\frac{-2B}{k_B T}\right) K(p, m|1, 3) \right. \\ &+ 5 \exp\left(\frac{-6B}{k_B T}\right) K(p, m|2, 0) + 7 \exp\left(\frac{-12B}{k_B T}\right) K(p, m|3, 1) \Big) \\ &+ \frac{1}{f_V(T)} \left( \exp\left(\frac{-0.5E_v}{k_B T}\right) K(p, m|0, 1) + \exp\left(\frac{-1.5E_v}{k_B T}\right) K(p, m|1, 0) \right) \end{aligned} \quad (7.21)$$



where  $f_B(T)$  and  $f_V(T)$  are the partition functions for rotational and vibrational states,

$$f_B(T) = 1 + 3 \exp(-2B/k_B T) + 5 \exp(-6B/k_B T) + 7 \exp(-12B/k_B T), \quad (7.22)$$

and

$$f_V(T) = \exp(-0.5E_v/k_B T) + \exp\left(\frac{-1.5E_v}{k_B T}\right) + \exp\left(\frac{-2.5E_v}{k_B T}\right). \quad (7.23)$$

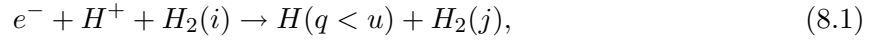
Higher terms in the partition functions are very small and have been cut off. Two-body cross sections for deexcitations are calculated by (7.16). Rate coefficients have been calculated up to  $K(60, 60)$  in both ways and detailed balance relation has been checked to every rate coefficient with it's reverse transition. Rate coefficient  $k(p, c)$  are also calculated with the similar expression. All rate coefficients then will be put into equation (7.5) to obtain the recombination coefficient.

# CHAPTER VIII

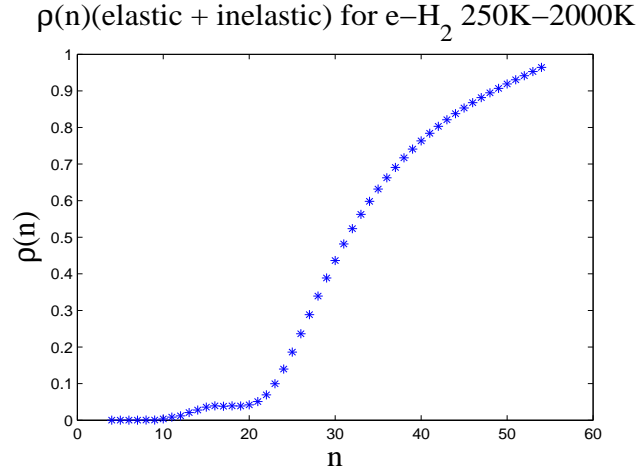
## RESULTS

### 8.1 *Results for Collision with $H_2$*

Again we take hydrogen molecule as the example of the calculation. For process



the temperature is set to be 250K. Differential cross sections are adopting the same data as we used in chapter 6. Equation (7.2) was used to calculate  $\rho(p)$ . When the level bounds are set to be  $u = 5$  and  $s = 54$ , the  $\rho'$ 's are shown in figure 8.1. The bump in the lower levels is due to the resonant transitions of the molecular excitation.



**Figure 8.1:** Rates passing level  $n_A$

Recombination coefficient  $\alpha_3$  is calculated using Bates' equation (3.17). When  $u = 5$  and  $s = 54$

$$\alpha_3 = 7.73 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1}. \quad (8.2)$$

Magnitude check (Byron bottleneck check) with a set of special  $\rho's$

$$\rho(n > n^*) = 1, \quad \rho(n < n^*) = 0, \quad (8.3)$$

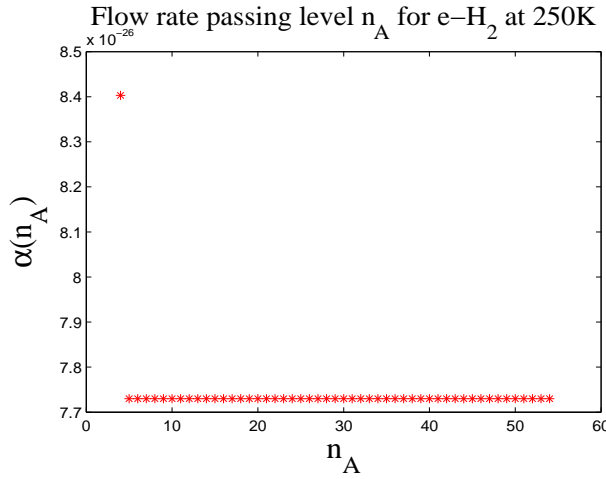
where  $n^*$  is about 25. The corresponding bottleneck rate  $\alpha_b$  is

$$\alpha_b = 3.4004 \times 10^{-25} \quad cm^6 s^{-1}. \quad (8.4)$$

The recombination coefficients passing level  $n_A$  was calculated using equations (7.5). They all have the same value

$$\alpha = 7.73 \times 10^{-26} \quad cm^6 s^{-1}, \quad (8.5)$$

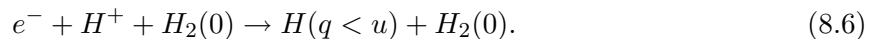
which is the same as the recombination coefficient calculated in Bates' equation. The figure 8.2 shows the results of  $\alpha's$ . The flat curve shows that the system is in the quasi-equilibrium condition and the rate flow is a constant. Since we have used some rate coefficient to obtain the reverse term, this flat curve also indicate that the detail balance is satisfied.



**Figure 8.2:** Rates passing level  $n_A$

### 8.1.1 Comparison to Elastic Collisions

The results with only the rates of elastic collision had been calculated to compare with the about results. For process



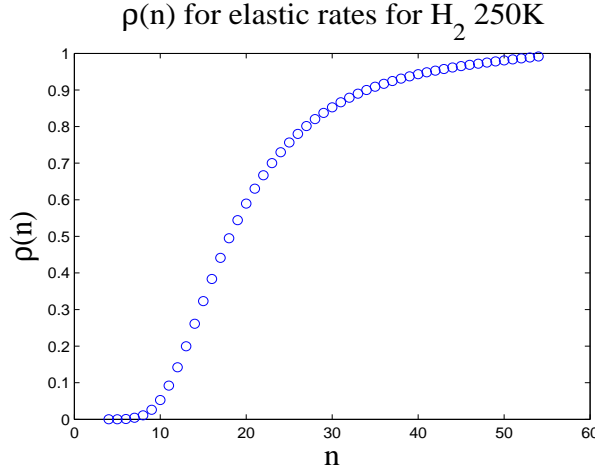
The rate coefficients  $K(p, m)$  and  $K(p, c)$  are replaced by the elastic term,

$$K(p, m) = K_0(p, m), \quad (8.7)$$

and

$$K(p, c) = K_0(p, c). \quad (8.8)$$

Equation (7.2) was used to calculate  $\rho(p)$ . When the level bounds are set to be  $u = 5$  and  $d = 54$ , the  $\rho'$ s are shown in figure 8.3.



**Figure 8.3:** Coefficient  $\rho(n)$

The curve of  $\rho$  is smooth whereas no resonant transition has happened. It has a smaller sink than the inelastic curve, which indicated that the electrons on the excited levels have a better chance to be re-ionized. So the function  $\rho(p)$  can be considered as the probability of being re-ionized.

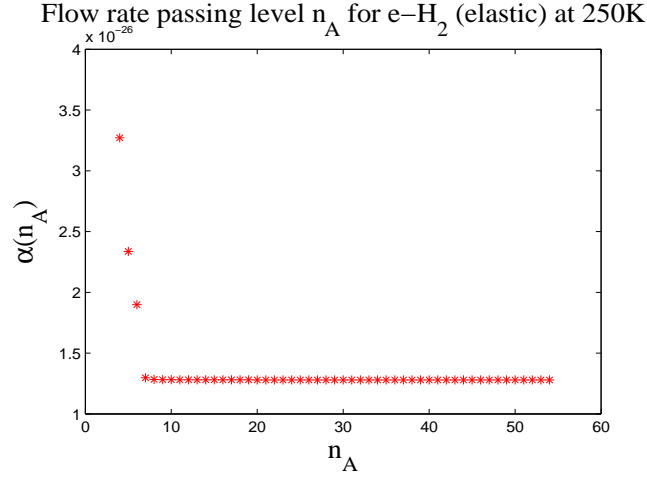
Recombination coefficient  $\alpha_3$  is calculated using Bates' equation (3.17). When  $u = 5$  and  $d = 54$

$$\alpha_3 = 1.2801 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1}. \quad (8.9)$$

The recombination coefficients  $\alpha$  passing level  $n_A$  is calculated using equations (7.5). They are all the same as the  $\alpha_3$  calculated above,

$$\alpha = 1.2801 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1}. \quad (8.10)$$

As we can see on the figure 8.4, the calculated  $\alpha$ 's below level  $u$  have certain “edge effect”. It is due to the fact that  $\rho(q < u)$  are not exactly zero. The point sit on the edge  $u = 4$  is the  $\alpha_3$  that we calculated above.. When we choose different  $u$ ,  $\alpha_3$  will vary a little and does not always equal to  $\alpha$ . On the contrary,  $\alpha$  is much more stable and we should use  $\alpha$  as the final results of recombination coefficient.



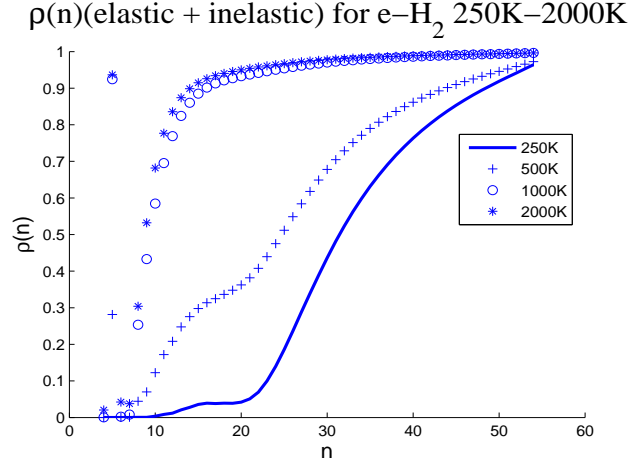
**Figure 8.4:** Flow rate passing level  $n_A$  in elastic collision.

### 8.1.2 Recombination Coefficients in Different Temperatures

Recombination coefficients in different temperatures were calculated for  $T = 250, 500, 1000$  and 2000. The number density distributions are shown below. It shows that with more thermal energy, the collision is more likely to happen and there are more electrons on the excited energy levels. Yet the “sink” of the recombination, the low energy levels that the trapped electrons are hard to escape from, is getting smaller. Recombination coefficients are shown in table 8.1.

The log of the recombination coefficients for different temperatures are shown in figure (8.6), which shows that the recombination coefficient are dropped quickly with temperature increased. This variation is assumed as a power law [9], and it is fitted with

$$\alpha(H_2) = 5.01 \times 10^{-26} \left( \frac{300}{T} \right)^{2.37} \text{ cm}^6 \text{ s}^{-1}. \quad (8.11)$$



**Figure 8.5:**  $\rho(p)$  for  $H_2T = 250 - 2000K$ .

**Table 8.1:** Results of recombination coefficients for different temperatures for  $H_2$ .

Temperature(K)	$\alpha(cm^6s^{-1})$
250	$7.73 \times 10^{-26}$
500	$2.09 \times 10^{-26}$
1000	$1.39 \times 10^{-27}$
2000	$7.98 \times 10^{-28}$

## 8.2 Results for Gases $N_2$ , $O_2$ , $CO$ , $CO_2$ , and $H_2O$

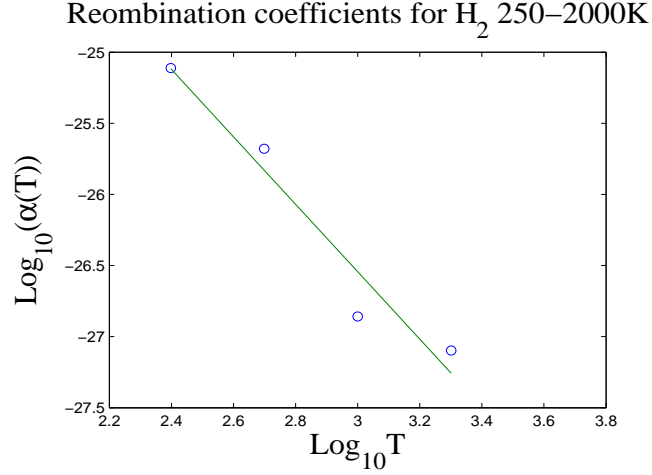
Similar work has done to molecules  $N_2$ ,  $O_2$ ,  $CO$ ,  $CO_2$ , and  $H_2O$  and similar results were observed. (figure (8.7)-(8.11)).

### 8.2.1 Results for $N_2$

Recombination coefficients are shown in table 8.2.

**Table 8.2:** Results of recombination coefficients for different temperatures for  $N_2$ .

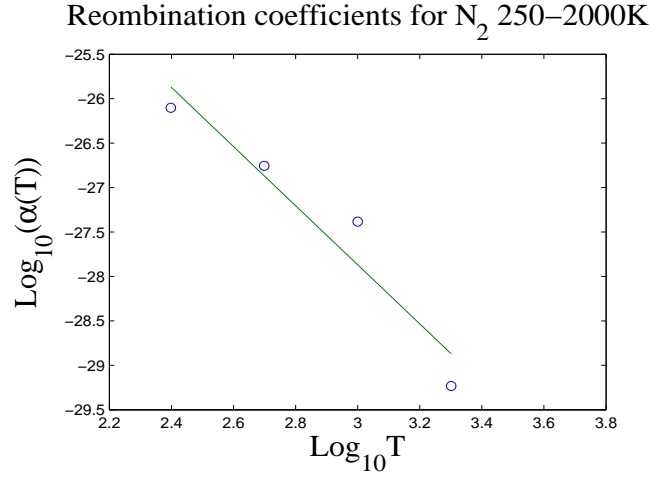
Temperature(K)	$\alpha(cm^6s^{-1})$
250	$7.89 \times 10^{-27}$
500	$1.75 \times 10^{-27}$
1000	$4.14 \times 10^{-28}$
2000	$5.86 \times 10^{-30}$



**Figure 8.6:** Log of recombination coefficients for  $H_2$ ,  $T = 250 - 2000K$ .

The log of the recombination coefficients for different temperatures are shown in figure (8.7), and it is fitted with

$$\alpha(N_2) = 7.41 \times 10^{-27} \left(\frac{300}{T}\right)^{3.33} \text{ cm}^6 \text{ s}^{-1}. \quad (8.12)$$



**Figure 8.7:** Log of recombination coefficients for  $e - N_2$ ,  $T = 250 - 2000K$ .

### 8.2.2 Results for $O_2$

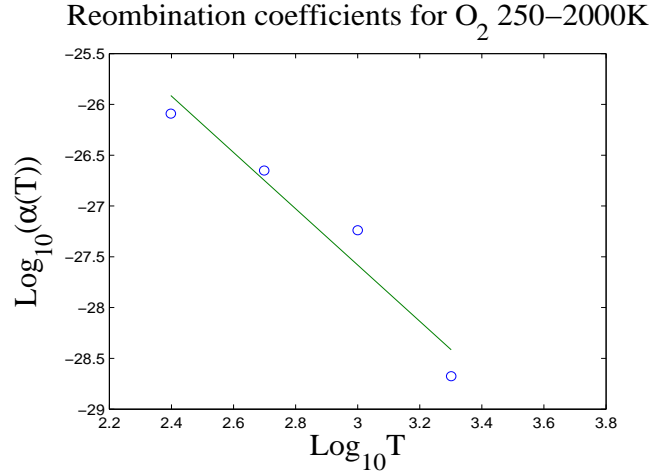
Recombination coefficients are shown in table 8.3.

**Table 8.3:** Results of recombination coefficients for different temperatures for  $O_2$ .

Temperature( $K$ )	$\alpha(cm^6s^{-1})$
250	$8.1 \times 10^{-27}$
500	$2.23 \times 10^{-27}$
1000	$5.77 \times 10^{-28}$
2000	$2.11 \times 10^{-29}$

The log of the recombination coefficients for different temperatures are shown in figure (8.8), and it is fitted with

$$\alpha(O_2) = 9.33 \times 10^{-27} \left(\frac{300}{T}\right)^{3.9} cm^6s^{-1}. \quad (8.13)$$



**Figure 8.8:** Log of recombination coefficients for  $e - O_2$ ,  $T = 250 - 2000K$ .

### 8.2.3 Results for $CO$

Recombination coefficients are shown in table 8.4.

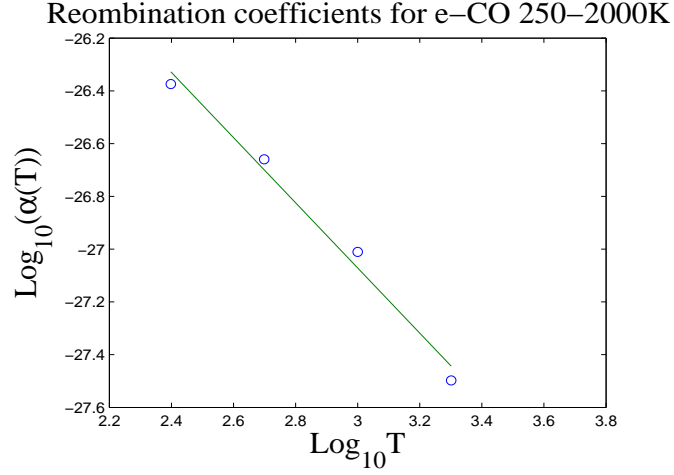
The log of the recombination coefficients for different temperatures are shown in figure (8.9), and it is fitted with

$$\alpha(CO) = 3.71 \times 10^{-27} \left(\frac{300}{T}\right)^{1.23} cm^6s^{-1}. \quad (8.14)$$



**Table 8.4:** Results of recombination coefficients for different temperatures for  $CO$ .

Temperature( $K$ )	$\alpha(cm^6s^{-1})$
250	$4.22 \times 10^{-27}$
500	$2.19 \times 10^{-27}$
1000	$9.76 \times 10^{-28}$
2000	$3.18 \times 10^{-28}$



**Figure 8.9:** Log of recombination coefficients for  $e - CO$ ,  $T = 250 - 2000K$ .

#### 8.2.4 Results for $CO_2$

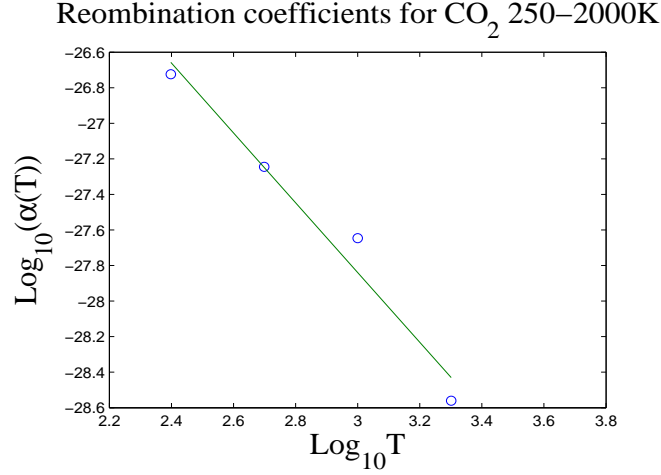
Recombination coefficients are shown in table 8.5.

The log of the recombination coefficients for different temperatures are shown in figure (8.10), and it is fitted with

$$\alpha(CO_2) = 1.55 \times 10^{-27} \left(\frac{300}{T}\right)^{1.96} cm^6 s^{-1}. \quad (8.15)$$

**Table 8.5:** Results of recombination coefficients for different temperatures for  $CO_2$ .

Temperature( $K$ )	$\alpha(cm^6s^{-1})$
250	$1.89 \times 10^{-27}$
500	$5.69 \times 10^{-28}$
1000	$2.26 \times 10^{-28}$
2000	$2.75 \times 10^{-29}$



**Figure 8.10:** Log of recombination coefficients for  $e - CO_2$ ,  $T = 250 - 2000K$ .

**Table 8.6:** Results of recombination coefficients for different temperatures for  $H_2O$ .

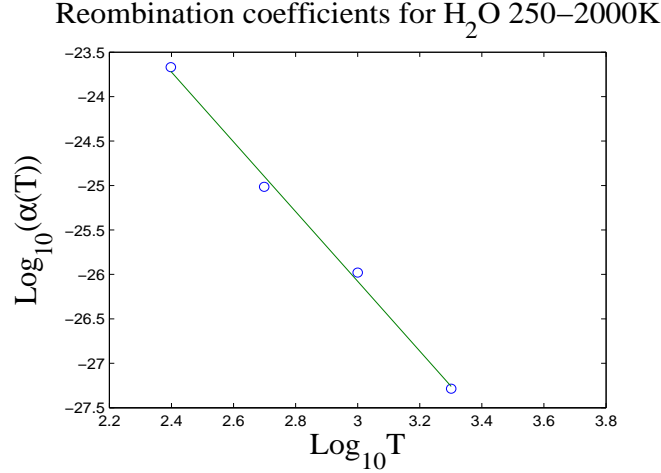
Temperature(K)	$\alpha(cm^6s^{-1})$
250	$2.14 \times 10^{-24}$
500	$9.66 \times 10^{-26}$
1000	$1.04 \times 10^{-26}$
2000	$5.17 \times 10^{-28}$

### 8.2.5 Results for $H_2O$

Recombination coefficients are shown in table 8.6.

The log of the recombination coefficients for different temperatures are shown in figure (8.11), and it is fitted with

$$\alpha(H_2O) = 9.33 \times 10^{-25} \left(\frac{300}{T}\right)^{3.93} cm^6 s^{-1}. \quad (8.16)$$



**Figure 8.11:** Log of recombination coefficients for  $e - H_2O$ ,  $T = 250 - 2000K$ .

**Table 8.7:** Results of  $e - N_a^+$  recombination coefficients for different temperatures for  $N_2$ .

Temperature( $K$ )	$\alpha(cm^6s^{-1})$
800	$2.14 \times 10^{-28}$
1600	$2.31 \times 10^{-30}$
3200	$3.92 \times 10^{-31}$
4500	$2.40 \times 10^{-31}$

### 8.3 Results with Metallic Ion $Na^+$

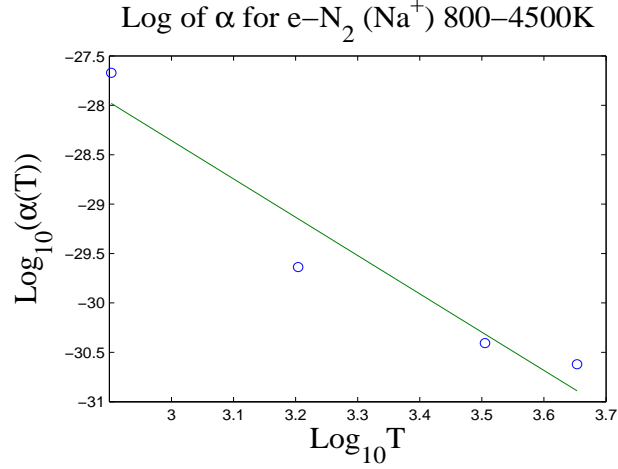
We also calculated the recombination coefficients for electrons recombining with  $Na^+$ . The ionization potential of the ion has changed to  $5.138eV$ . The molecular gases in which we are interested are  $N_2$ ,  $O_2$ ,  $CO$ ,  $CO_2$ , and  $H_2O$ . Temperatures have been set as  $800K$ ,  $1600K$ ,  $3200K$ , and  $4500K$ .

#### 8.3.1 Results for $N_2$

Recombination coefficients are shown in table 8.7.

The log of the recombination coefficients for different temperatures are shown in figure (8.12), and it is fitted with

$$\alpha(N_2) = 4.67 \times 10^{-27} \left(\frac{300}{T}\right)^{3.88} cm^6s^{-1}. \quad (8.17)$$



**Figure 8.12:** Log of recombination coefficients for  $e - N_2$ , ( $N_a^+$ ),  $T = 800 - 4500K$ .

**Table 8.8:** Results of  $e - N_a^+$  recombination coefficients for different temperatures for  $O_2$ .

Temperature(K)	$\alpha(cm^6s^{-1})$
800	$1.73 \times 10^{-27}$
1600	$1.23 \times 10^{-28}$
3200	$2.33 \times 10^{-29}$
4500	$1.13 \times 10^{-29}$

### 8.3.2 Results for $O_2$

Recombination coefficients are shown in table 8.8.

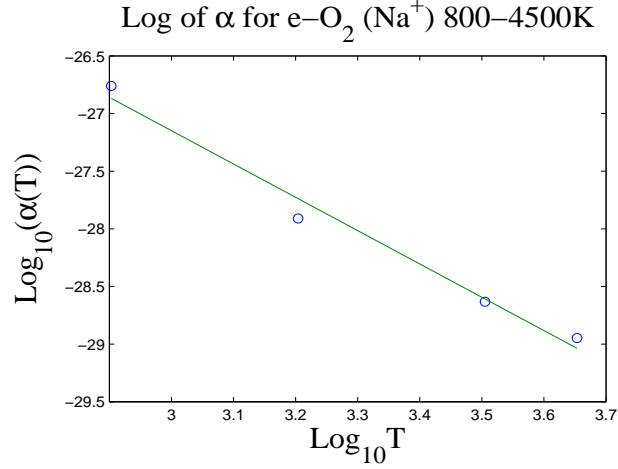
The log of the recombination coefficients for different temperatures are shown in figure (8.13), and it is fitted with

$$\alpha(O_2) = 2.29 \times 10^{-26} \left(\frac{300}{T}\right)^{2.89} cm^6s^{-1}. \quad (8.18)$$

### 8.3.3 Results for $CO$

Recombination coefficients are shown in table 8.9.

The log of the recombination coefficients for different temperatures are shown in figure



**Figure 8.13:** Log of recombination coefficients for  $e - O_2$ ,  $(N_a^+)$ ,  $T = 800 - 4500K$ .

**Table 8.9:** Results of  $e - N_a^+$  recombination coefficients for different temperatures for  $CO$ .

Temperature( $K$ )	$\alpha(cm^6 s^{-1})$
800	$1.10 \times 10^{-27}$
1600	$5.78 \times 10^{-29}$
3200	$1.92 \times 10^{-29}$
4500	$1.17 \times 10^{-29}$

(8.14), and it is fitted with

$$\alpha(CO) = 8.71 \times 10^{-27} \left(\frac{300}{T}\right)^{2.57} cm^6 s^{-1}. \quad (8.19)$$

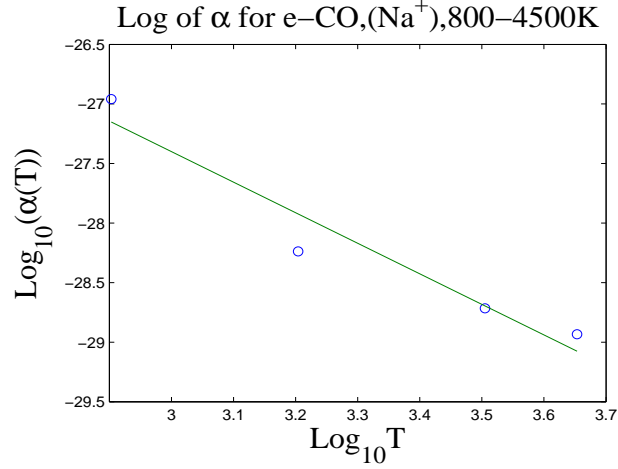
### 8.3.4 Results for $CO_2$

Recombination coefficients are shown in table 8.10.

The log of the recombination coefficients for different temperatures are shown in figure

**Table 8.10:** Results of  $e - N_a^+$  recombination coefficients for different temperatures for  $CO_2$ .

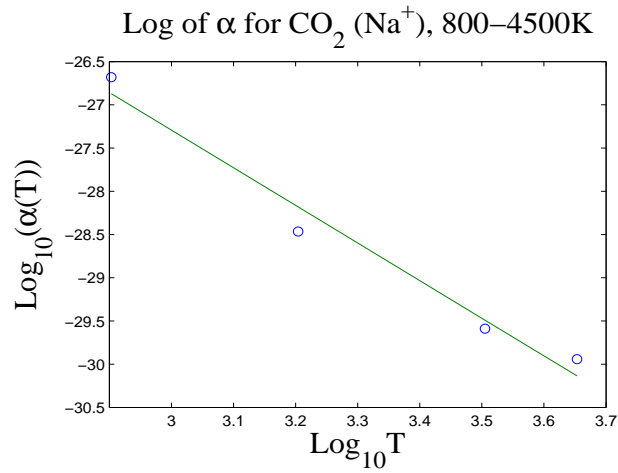
Temperature( $K$ )	$\alpha(cm^6 s^{-1})$
800	$2.08 \times 10^{-27}$
1600	$3.42 \times 10^{-29}$
3200	$2.58 \times 10^{-30}$
4500	$1.14 \times 10^{-30}$



**Figure 8.14:** Log of recombination coefficients for  $e - CO$ ,  $(N_a^+)$ ,  $T = 800 - 4500\text{K}$ .

(8.15), and it is fitted with

$$\alpha(CO_2) = 9.54 \times 10^{-26} \left(\frac{300}{T}\right)^{4.35} \text{ cm}^6 \text{ s}^{-1}. \quad (8.20)$$



**Figure 8.15:** Log of recombination coefficients for  $e - CO_2$ ,  $(N_a^+)$ ,  $T = 800 - 4500\text{K}$ .

### 8.3.5 Results for $H_2O$

Recombination coefficients are shown in table 8.11.

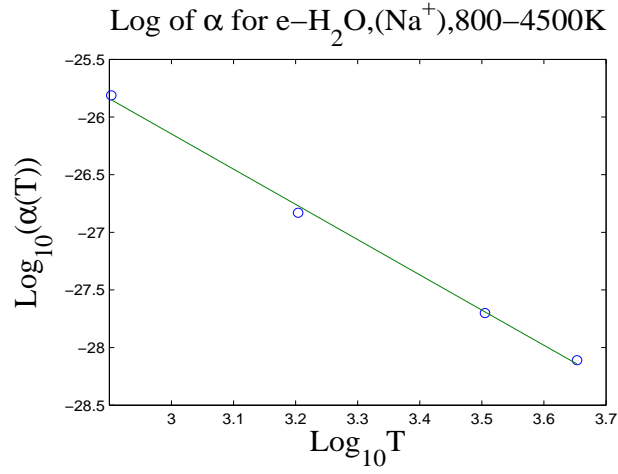
The log of the recombination coefficients for different temperatures are shown in figure

**Table 8.11:** Results of  $e - N_a^+$  recombination coefficients for different temperatures for  $H_2O$ .

Temperature(K)	$\alpha(cm^6s^{-1})$
800	$1.54 \times 10^{-26}$
1600	$1.48 \times 10^{-27}$
3200	$1.99 \times 10^{-28}$
4500	$7.76 \times 10^{-29}$

(8.16), and it is fitted with:

$$\alpha(H_2O) = 2.82 \times 10^{-25} \left(\frac{300}{T}\right)^{3.06} cm^6s^{-1} \quad (8.21)$$



**Figure 8.16:** Log of recombination coefficients for  $e - H_2O$  ( $N_a^+$ ),  $T = 800 - 4500K$ .

## CHAPTER IX

### CONCLUSION

We have extended the quantum impulse approximation theory to the inelastic collision. The theory makes it possible for us to establish a direct connection from the quantum scenario to its classical correspondence.

We are able to calculate the total inelastic cross sections for the degenerated states with different angular momenta. It is also shown that this theory is symmetric in the initial and final states such that it satisfies the principle of detailed balancing perfectly. It was proved that summing over the transitions  $nl \rightarrow n'$  and  $nl \rightarrow n'l'$  would give us the total cross section of transition  $n \rightarrow n'$ . The new results matched well with the binary encounter results, which was previously used to calculate the cross section in the classical method.

Rate coefficients were calculated for the common gases in the atmosphere being the third particle. The resonant effect of the rate coefficients had been observed. As the rotational or vibrational excitations match with the energy lost of the electron transition, the rate coefficients are large and the recombination is likely to happen in this channel. Therefore the inelastic rate coefficients make important contributes in collisional recombination. Detailed balance relation were also proved for rate coefficients and thus we could substitute a rate coefficient with its reverse process.

Recombination coefficients were then calculated in terms of rate coefficients. Bates' calculation were carried out in compare with the net rate flow through a certain excited levels, which were found to be more stable and reflected a clearer picture of the whole process. Results have been compared with the elastic collision, and we found a much larger possibility for the recombination to happen in inelastic collisions.

A dramatic decreasing of rates when temperature increased was also observed. More thermal energy increases the probability of electrons for being re-ionized, which means



number density distribution is raised and the sink is smaller.

Similar calculations had been carried out for the upper atmosphere gases, such as  $N_2$ ,  $O_2$ ,  $CO$ ,  $CO_2$ , and  $H_2O$ . The hydrogen nucleus can also be replaced with other metallic ion. Similar conclusions were made by these calculations.

The input data we have collected are the two-body cross sections for electron-molecular collision. Various sources gave various data. For some of them, such as  $O_2$ , we are still lack of appropriate data for low energy collisions. The calculations and the experiments are still carrying on in finding these data. There sure left lots to do for us.

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## VITA

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